Synthesis and Characterization of Thermoplastic Polymers

By

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Abstract.

This research is focused on the synthesis and characterizations of polyaromatic ethers using *meta-*, *para-*, and *ortho*-dichloro complexes of cyclopentadienyliron. First of all, polyaromatic ethers are a class of polymers that have received a considerable amount of attention due to their high-performance properties. These properties involve outstanding thermal and chemical stability, leading these polymers to be suited for high-temperature applications. Second, the incorporation of cationic η^6-chloroarene-η^5-cyclopentadienyliron moieties can facilitate nucleophilic aromatic substitution reactions due to the intense electron-withdrawing ability of the monomers. Finally, the objective of this work was to investigate the solubility of both monomers and the effect of the different aliphatic length of diols when reacted with the iron complexes. It was concluded that as length of diols increases, the solubility of both monomers and polymers increases as well. It was also found that these polymers showed good thermal stability.

Acknowledgements.

This thesis has become a reality with the kind support and help of many individuals. I would like to extend to my sincere thanks to all of them.

First and foremost, thanks to Allah almighty whom enabled me to research on such a hot issue of these days. I reverse the patronage and moral support extended with love, by my parents (Mr., Abdulhmeed Al-Tamimi & Mrs. Rahmah Almuhammadi), my brothers and my sister whose passionate encouragement made it possible for me to complete this project.

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Thank you to all the members of my student advisory committee including Dr. Rabin Bissessur and Dr. Nola Etkin. My research would not have been as fruitful without their guidance and incredible insight.

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I am at a total loss of words in expressing the depth of my emotion for my wife Mrs. Shouq Almuhammadi, for her constant love, support and inspiration.

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Abbreviations

Ar	aryl
*Ar	complexed aryl
br	broad
^{13}C	carbon-13
conc.	concentrated
°C	degrees Celsius
Cp	cyclopentadienyl ring
Cp*	Pentamethylcyclopentadiene
δ	chemical shift
d	doublet
dd	doublet of doublets
DCC	N, N'-dicyclohexylcarbodiimide ($C_{13}H_{22}N_2$)
DCU	N, N'-dicyclohexylurea ($C_{13}H_{24}N_2O$)
DMAP	4-dimethylaminopyridine ($(CH_3)_{2NC5H4N}$)
DMF	N,N-dimethylformamide
DMSO	dimethyl sulfoxide
PEG	Polyethylene glycol
ROP	Ring opening polymerization
S_NAr	NucleophiIic aromatic substitution

eq.	Equivalents
g	grams
^{1}H	proton
h	hours
Hz	Hertz (s^{-1})
J	coupling constant (in spectroscopy; Hz)
L	litre (10^{-3} m^{-3})
M	molar ($mol \cdot L^{-1}$)
m	meta
Me	methyl
min	minutes
mL	millilitre ($10^{-3}L$)
mmol	millimole (10^{-3} mole)
mol	mole ($6.022 \cdot 10^{-23}$ particles)
NMR	nuclear magnetic resonance
o	ortho
p	para
m	meta
ppm	parts per million
q	quartet

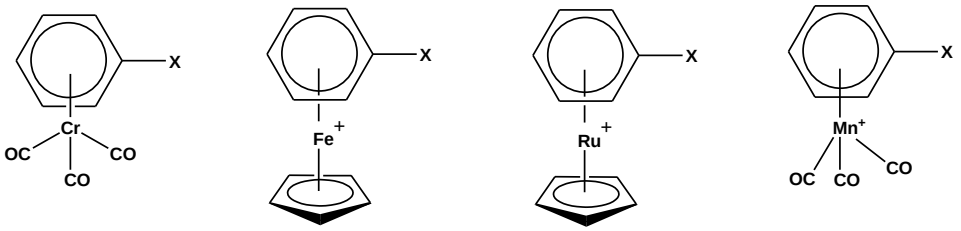
RBF	round bottom flask
s	singlet
t	triplet

1.Chemistry of Organic Arene Complexes

1.1 Introduction:

Over the past few decades, the synthesis of organometallic arene complexes, in particular the preparation of new compounds having transition metals coordinated to arene moieties, has attracted a great deal of attention. The majority of the work in this area has been concentrated on the design of arenes coordinated to $Cr(CO)_3$, $Mo(CO)_3$, $Mn(CO)_3$,$CpFe^+$ and Cp*Ru because of their electron withdrawing ability which facilitates the nucleophilic aromatic substitution as well as addition reaction on the arene motifs. [1-18] The use of cyclopentadienyliron ($CpFe^+$), chromium tricarbonyl $Cr(CO_3)$ and manganese tricarbonyl $Mn(CO)^+_{3,}$ and cyclopentadienyl ruthenium ($CpRu^+$) moieties in the activation of the aromatic compound have been extensively investigated. [11,13,14] Mechanistic research concerning the reactivity of some halobenzene metal complexes towards nucleophilic aromatic substitutions with methoxide ion has allowed for a comparison of the electron-withdrawing capability of the metal moieties with respect to one another. Figure 1.01 represents the relative electron-withdrawing power of some of the metal moieties indicated above. [19] A one-dimensional examination of the different metal moieties relies on their capacity to activate aromatic compounds towards

nucleophilic reactions, with $Mn(CO)_3$ being the most favorable. However, the use of $Mn(CO)_3$ has been restricted due to its tremendous cost and high degree of toxicity.[6-10,14,20,21]



numeric estimation of the reactivity	**<< 1 very small**	**1**	**1**	**10^3**

Figure 1.01: relative electron-withdrawing ability of metallic moieties upon π-complexation to an aryl halide.

Arene iron complexes have been widely investigated because of their intense electron withdrawing ability, which arises from the positive charge on the iron center and makes nucleophilic substitution and addition reaction on the arene ring easier. [4,5,15] This thesis will focus on the use of arene cyclopentadienyliron complexes in the design of functionalized polyaromatic ethers and investigate the solubility of both monomers, polymers, and the effect of the different aliphatic length of diols reacted with the iron complexes.

1.2 Synthesis and Reactivity of η^6-Arene- η^5-cyclopentadienyliron Complexes

1.2.1 Synthesis.

The chemistry of $CpFe^+$ complexes has been actively tracked over the last few decades. Applications to organic and polymer synthesis as well as supramolecular chemistry have been identified. Figure 1.02 demonstrates several chemical reactions of these molecules including nucleophilic addition and substitution, oxidation of substituents, redox reactions, and photolytic cleavage. Recent reviews by Astruc have outlined the many functions and potential applications of these cationic complexes. [18,19] The focus of this present study will be on double nucleophilic aromatic substitution reactions.

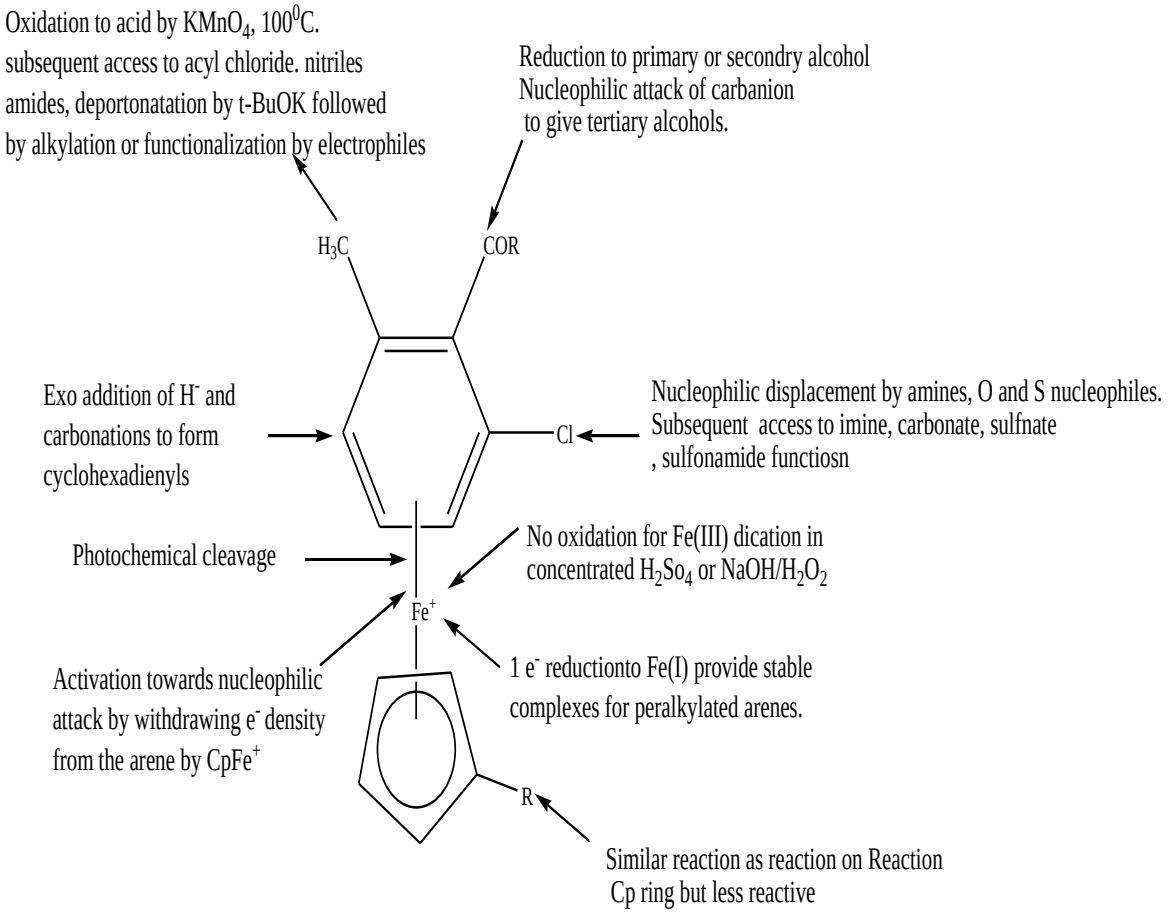
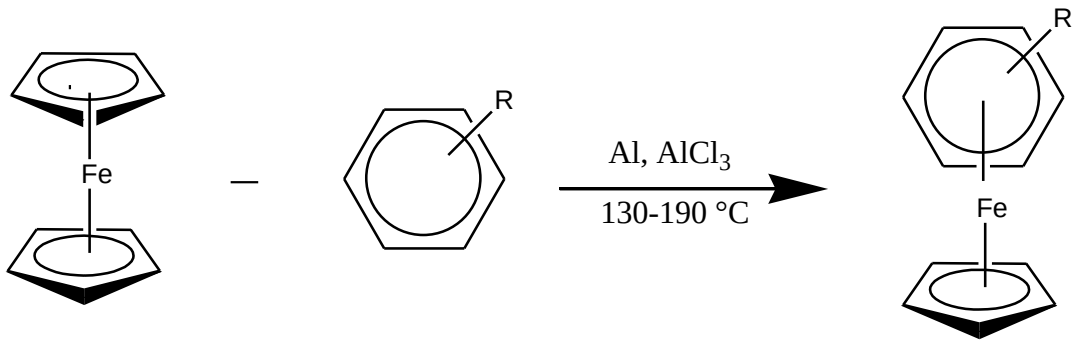


Figure 1.02: Different kinds of chemistry at the organoiron center.

There are many procedures that have been improved upon in order to synthesize arene cyclopentadienyl complexes over the last two decades. Coffield and coworkers published the first cyclopentadienyl iron in 1957. [2] In this method, the reaction of refluxing mesitylene with cyclopentadienyliron dicarbonyl chloride took place in the presence of aluminum chloride. The desired product was removed as iodide salt. Although this method of preparation of pentamethylcyclopentadienyliron complexes of variable arenes under the equivalent designated condition yielded the desired product, many difficulties such as low final yields and formation of ferrocenium cation as a byproduct remained.[4,22,23]

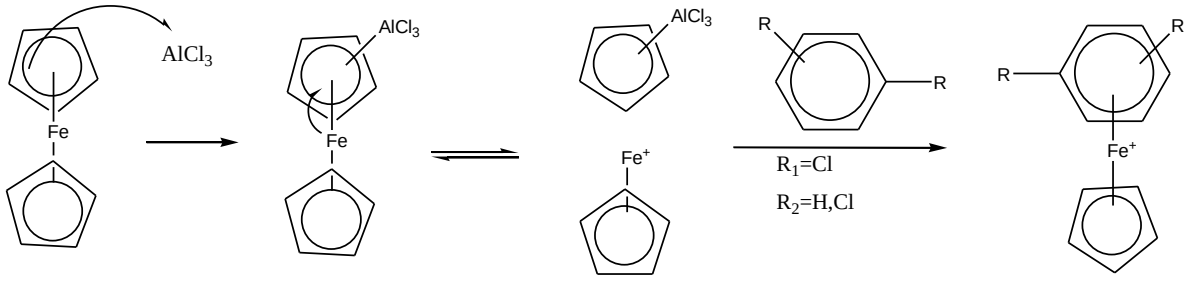


Scheme 1.01: The synthesis of η^6-arene-η^5-cyclopentadienyliron complexes via ligand exchange.

Shortly thereafter, Nesemeyanov and coworkers published two important articles, [24,25] in which arene cyclopentadienyliron complexes were synthesized via ligand exchange reaction of ferrocene and arene. The reaction took place at high temperatures (70-190°C) for 1-16h depending on the arene used and aluminum powder was added to the reaction to prevent the oxidation of ferrocene to the ferrocenium cation. Because of the higher temperature of these reactions, arene substrate, or inert solvents such as decalin, cyclohexane or methylcyclohexane, were used. This procedure is the most common and efficient route for synthesizing different cyclopentadienyliron complexes.

Aluminum chloride is the most effective Lewis acid used as a catalyst to induce this ligand exchange reaction. The percentage of the desired complex is highly affected by the nature of arene; arenes containing electron-donating groups can be obtained in much higher yields and under mild conditions. Furthermore, the yields of the reaction were dependent on the relative amount of aluminum chloride and ferrocene. As the amount of ferrocene increases, the yields of this reaction decrease significantly. In order to yield the greatest amount of the desired product, a ratio of ferrocene/arene/$AlCl_3$/Al: 1:1:2:1 .In addition, it was found that the yield was enhanced from approximately 40 to 90%, by using the addition of small amount of either water or hydrochloric acid. [26] The mechanism of these ligand exchange reaction between ferrocene

and arenes have been explored by Astruc's and Sutherland's research groups. [27] The proposed mechanism has been illustrated in Scheme 1.02. The discovery of a ferrocene moiety before and after the hydrolysis of the reaction was a crucial step for proposing this mechanism.



Scheme 1.02: The proposed mechanism of the ligand exchange reaction

As shown in Scheme 1.02, coordination between $AlCl_3$ and one of the ferrocene Cp rings resulted in weakening one of the metal-Cp bonds and allowed for the cleavage of $CpFe^+$ moiety that subsequently coordinated to the arene ring.

In 1993, Dabirmanesh et al. reported on a new improved synthetic strategy to prepare arene cyclopentadienyliron complexes. [28-30] In this methodology, microwave dielectric heating was utilized to cause the ligand exchange of ferrocene. The advantages of this method include short reaction time and higher yields. Furthermore, these conditions allowed for the

production of complexes that could not be formed utilizing traditional methods. For instance, the ligand exchange of ferrocene with arene having bulky alkyl substituent, phenol, benzyl alcohol and benzaldehyde can be achieved by the microwave technique. A limitation of this methodology is the smaller scale of these reactions.

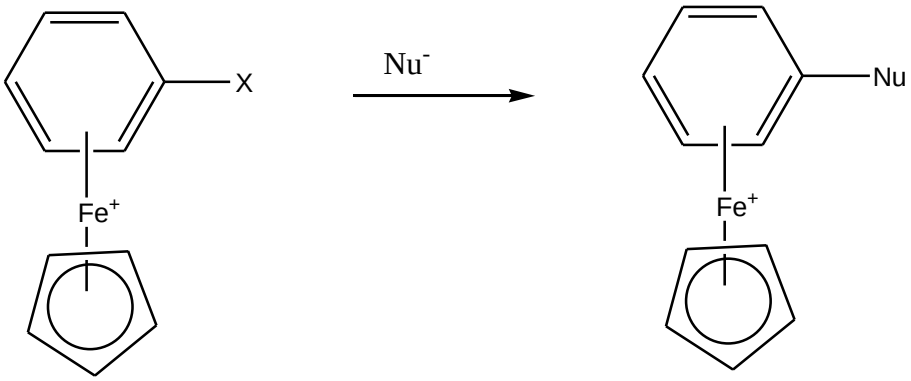
1.2.2 Nucleophilic Aromatic Substitution Reactions

The activity of arene group towards nucleophilic aromatic substitution increases due to the electron withdrawing nature of the cyclopentadienyliron moiety. In general, an aromatic substitution reaction of chlorobenzene with phenol needs long reaction times, high temperature and pressure or harsh catalyst. On the other hand, phenolic groups in the presence of weak bases such as K_2CO_3 readily substitute η^6-chlorosubstituted-arene-η^5-cyclopentadienyliron complexes at 25°C (Figure 1.03).. The wide variety of chemical reactions that η^6-arene- η^5-cyclopentadienyliron complexes can undergo, including reactions with either of the complexed rings, their substituents or the iron itself, thoroughly illustrates their noteworthy reactivity. [18] These complexes are susceptible to photolytic cleavage, oxidation and reduction reactions and nucleophilic addition and substitution reactions. The reactivity of these complexes toward nucleophilic aromatic substitution

reactions is the backbone for this research and will therefore be the essence of the following discussion.

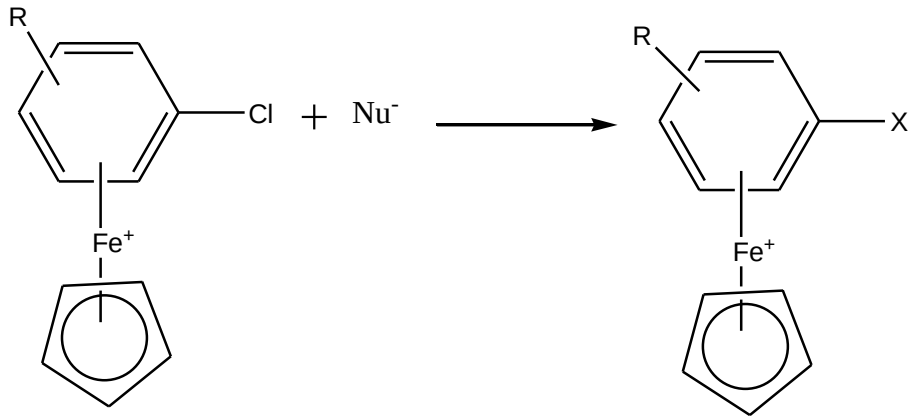
According to traditional organic chemistry, aromatic compounds are easily susceptible to electrophilic attack and, in the presence of one or more electron withdrawing substituents, are equally prone to act as electron acceptors and undergo reaction in the presence of nucleophile. The ability for an organometallic species such as CpFe to work as a strong electron-withdrawing group and activate a complexed arene toward nucleophilic attack was initially studied and published by Nesmeyanov and his coworkers in 1967. [31] They determined the activation of this metallic moiety to be comparable to that of two nitro groups. It was also shown that chloroarenes when complexed to $CpFe^{+}$ would be able to undergo nucleophilic aromatic substitution in the presence of a variety of carbon, oxygen, sulfur and nitrogen nucleophiles under fairly mild reaction conditions. [17] Subsequent consideration of η^6-arene- η^5-cyclopentadienyliron complexes has discovered the nucleophilic substitution of nitro-substituted arenes in the presence of a nucleophile, a proper base, and an appropriate reaction solvent. Scheme 1.03 represents a general strategy outlining the nucleophilic aromatic substitution reaction of nucleophiles with η^6-arene- η^5-cyclopentadienyliron complexes.

The use of this methodology for the synthesis of important organic precursors as well as species with biological or industrial potential demonstrates its synthetic utility. Specifically, both mono- and disubstituted chlorobenzene $CpFe^+$ complexes have successfully undergone S_NAr reactions in the presence of a number of carbanion nucleophiles and are seen as a viable route to carbon-carbon bond formation. [15,32-36] (Scheme 1.04). A notable advantage of this synthetic strategy is the option of preparing either symmetric or asymmetric derivatives by the successive substitution of dichlorobenzene complexes with nucleophiles which may be the same or different.



X= Cl, NO_2

Scheme 1.03: Nucleophilic substitution of cyclopentadienyliron activated chloro-and nitro-substituted arenes.



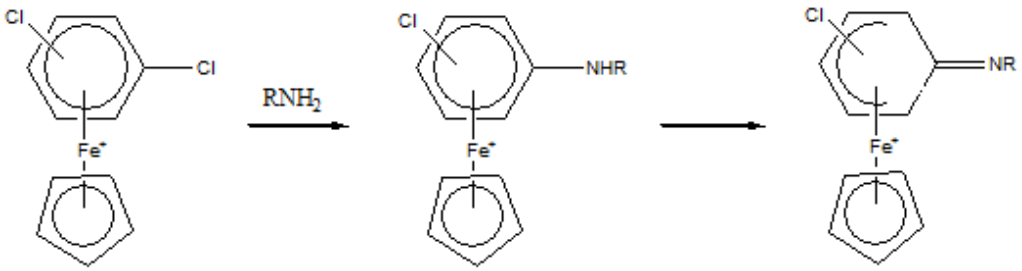
R= H,CH_3,Cl

Nu^-= (CN)CH(SO_2Ph)
(CN)CH(CO_2Et)
(CN)C(Et)(CO_2Et)
MeCH(CO_2Et)

Scheme 1.04: Reaction of a variety carbanion nucleophiles with η^6-(chloroarene) - η^5-cyclopentadienyliron complexes.

Helling and Hendrickson, who reported exclusive monosubstitution in the presence of primary amines, have investigated nucleophilic aromatic substitution of η^6-dichloroarene-η^5-cyclopentadienyliro complexes with nitrogen nucleophiles in some detail. [37,38] The rationale suggested for this observation was the formation of a zwitterionic cyclopentadienyliron complex possessing an exocyclic double bond. The production of these electron rich complex results from the deprotonation of an a-XH group (X = C, N, O, S) bonded to the complexed aromatic ring of a π-complex under basic reaction

conditions and renders the complex inactive toward further nucleophilic substitution (Scheme 1.05).

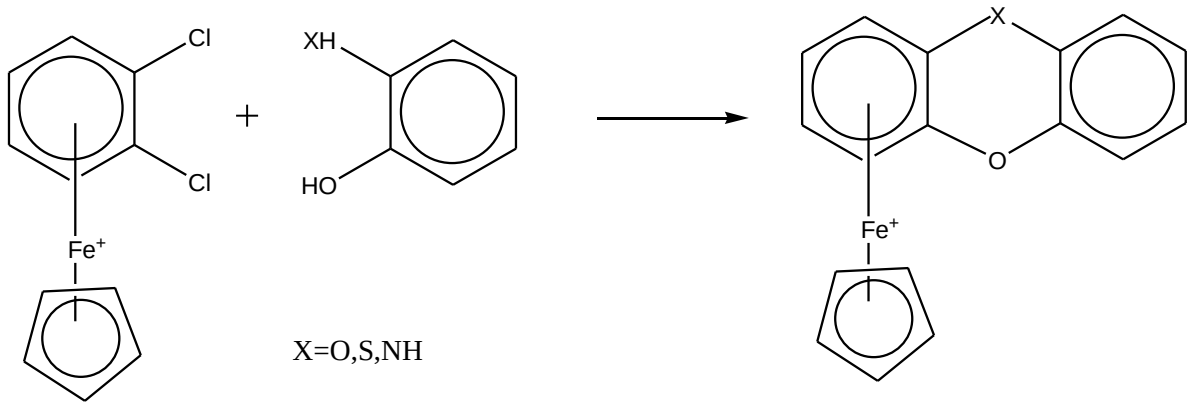


Scheme 1.05: Zwitterion Production.

A similar route cause by the reaction of η^6-dichloroarene-η^5-cyclopentadienyliron complexes with carbon nucleophiles possessing a methane proton. The lack of reactivity of the second chloro substituent on the complexed arene ring has been overcome in the case of primary amines upon the addition of an appropriate amount of acetic acid to the reaction. Selective substitution of dichloro arene complexes may be successfully prepared in the presence of secondary amine nucleophiles. The nitro group is known to be a better-leaving group than chlorine and as a result (nitroarene)$CpFe^+$ derivatives have been applied for nucleophilic aromatic substitution reactions with amines.

In addition to the above-illustrated carbon and nitrogen nucleophiles which have been shown to undergo substitution with (chloroarene) $CpFe^+$ complexes, the production of etheric and thioethenc Iinkages also takes place in the presence of oxygen and sulfùr nucleophiles. The double nucleophilic substitution reaction of a variety of oxygen, sulfur, and nitrogen containing 1,2-dinucleophiles with 1,2-substituted dichloroarenes shows a unique procedure to heterocyclic systems (Scheme 1.06).

The reaction of (chloroarene)$CpFe^+$ complexes with a variety of aliphatic and aromatic oxygen dinucleophiles has been investigated widely resulting in the synthesis of mono-, π- and polymetallic species.



Scheme 1.06: Reaction of 1,2-dinuclophiles with η^6-o-dichloroarene-η^5-cyclopentadienyliron complexes in heterocyclic production

1.2.3 NMR Studies of η^6-Arene- η^5-cyclopentadienyliron Complexes.

The coordination of organoiron moieties to arenes provides an outstanding procedure of analysis with ^{1}H NMR and ^{13}C NMR spectroscopy. In the ^{1}H NMR and ^{13}C NMR analysis, the resonance of the non-complexed arene appears at a significantly higher chemical shift than the complexed arene[39] For instance, when the ^{1}H NMR spectrum of *p*-dichlorobenzene and η^6-arene-η^5-cyclopentadienyliron hexafluorophosphate is compared with *p*-dichlorobenzene, the proton resonances caused by dichlorobenzene appears at 7.54 ppm whereas the proton resonances in the complexed arene of η^6-arene-η^5-cyclopentadienyliron appears at 7.04 ppm. The destabilization of anisotropy of the arene occurs because of coordination of the system to the iron center, which gives an upfield shift in the signal of the ^{1}H NMR spectrum due to the electron withdrawing nature of the cyclopentadienyliron moieties. These particular resonances can be used to determine if the reaction was successful due to the variation between the resonances of complexed arene versus uncomplexed arenes. [39-42]

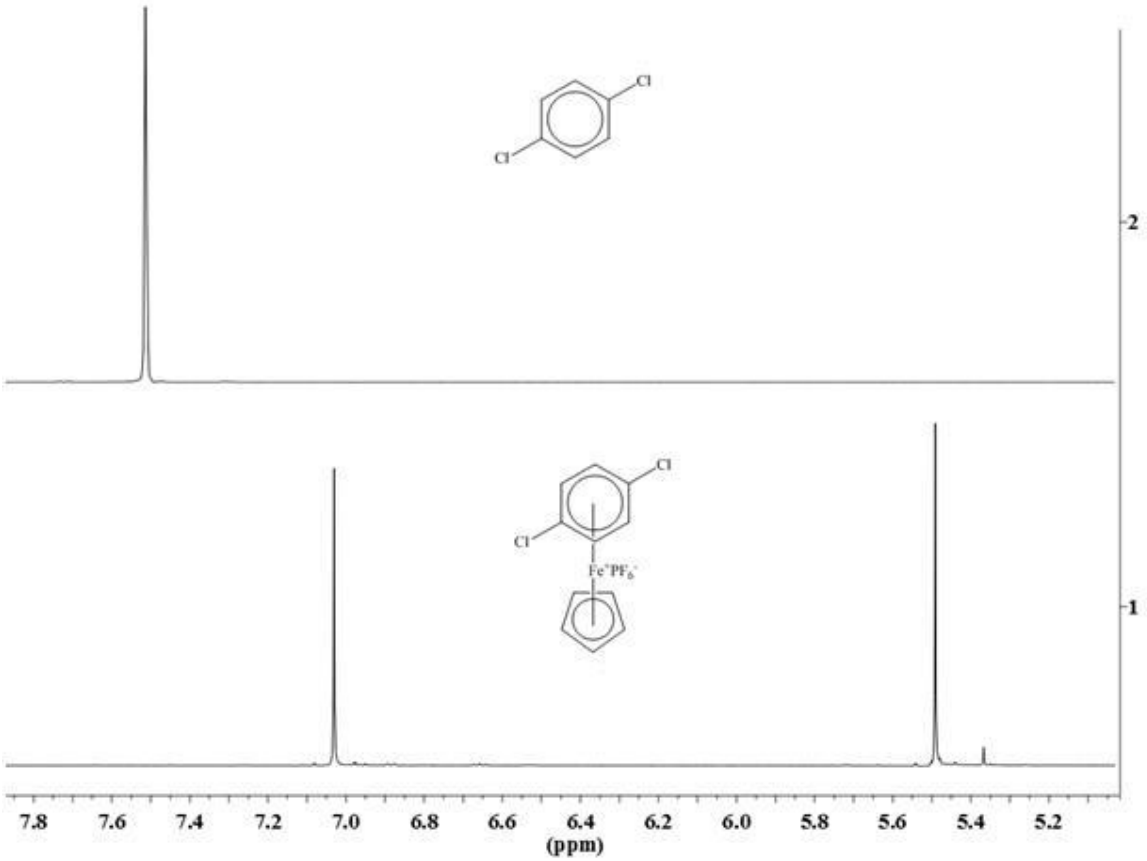


Figure1.03 : The ^{1}H NMR of complex (spectrum 1) and 1,4 dichlorobenzene (spectrum 2).

1.2.4 Photolytic Demetallation of $Fe^{+}Cp$ Moiety.

The ease of synthesis of arene cyclopentadienyliron complexes and their high reactivity to nucleophiles makes these materials outstandingly useful in organic synthesis. However, it is very important that cyclopentadienyliron complexes are able to be decomposed in order to obtain the desirable arene in high yield, which makes the metal-mediated procedure valuable. The decomposition of these complex moieties from the arenes have been conducted

using different methodologies in order to isolate their organic analogs. Decomplexation investigations of arene complexes have been conducted using a various of procedures, the most common being photolysis, pyrolysis, and electrolysis.

Pyrolysis, or thermal decomplexation, can be achieved be either heating the arene complex in high boiling point solvent such as DMSO or by heating the complex under vacuum. Because of the harsh condition of this procedure, the liberation of modified arene was highly influenced by their thermal stability. Utilizing microwave dielectric heat, Robert and coworkers have also described the decomplexation of arene complexes in a microwave.[34,43-45]

The second technique is electrolysis of cyclopentadienyliron arene. In contrast to pyrolysis, the procedure is carried out under milder conditions, resulting in the successful isolation of thermally unstable arenes. This reaction was found to be a result of the electrochemical reduction of cationic $18e^-$ complexes to their 19 e^- analogues, which subsequently undergo coordination solvent molecules resulting in the isolation of the free easily reduced compounds, could not be obtained using the same conditions.

Nesmeyanov achieved the cleavage of the cyclopentadienyliron moieties utilizing photolytic techniques.[39] Since then, photolysis has been considered to be the most common method of separating modified arenes from their organoiron complexes. In this technique, photolysis of the metallic compounds has occurred using sunlight or UV irradiation and results in the compound breaking down to ferrocene, iron salt, and free arene. Purification of the arene from the byproducts was accomplished by using either column chromatography or extraction. These techniques have the advantage of liberating temperature and electrochemical-sensitive arenes in excellent yields.[46-50]

The mechanism of these reactions was observed to be controlled by two portions: the applied solvent and the counter ion. Solvents with high nucleophilicity enhance the rates of the reaction and the yields of the products. In the absence of coordinating solvents, the presence of counter ion of the metal complexes led to increasing the quantum yields. Both of these effects could be connected to the coordination of the solvents or the counter ion to the metal atom and subsequently forming intermediate complexes. The contribution of the solvent and the counter ion was discovered to be in the

following order: $H_2O \approx$ propylene carbonate $\approx CH_3OH \geq CH_3CN > CF_3SO^-_3 > BF_3^- > Br^- \approx ClO_4^- >> PF^-_6 > CH_2Cl_2 \approx AsF^-_6 \approx SbF^-$.

In 1989, Schuster's group suggested a mechanism for the photolytic liberation of arenes from their organoiron complexes (Scheme1.07 and Scheme 1.08). [49] The authors proposed that first irradiation of arene cyclopentadienyliron complexes resulted in their excitation to the triplet state, which subsequently gave rise to ring slippage of the arene from η^6 to η^4 and opened a coordination site at the iron atom. Either the solvent or the counter ion forming an intermediate complex, which decomposed to generate ferrocene and different iron salts, then occupied this coordination site.

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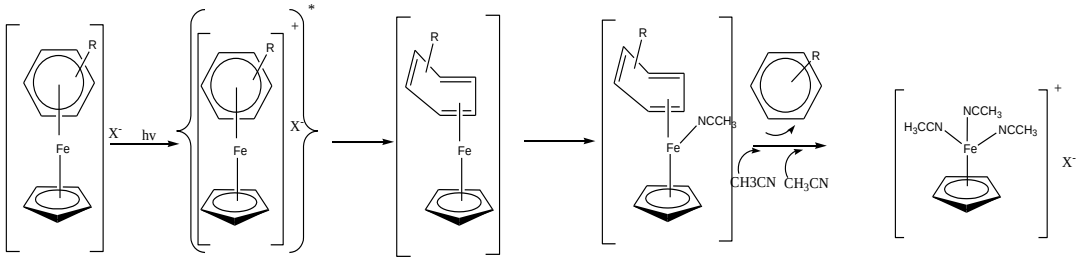
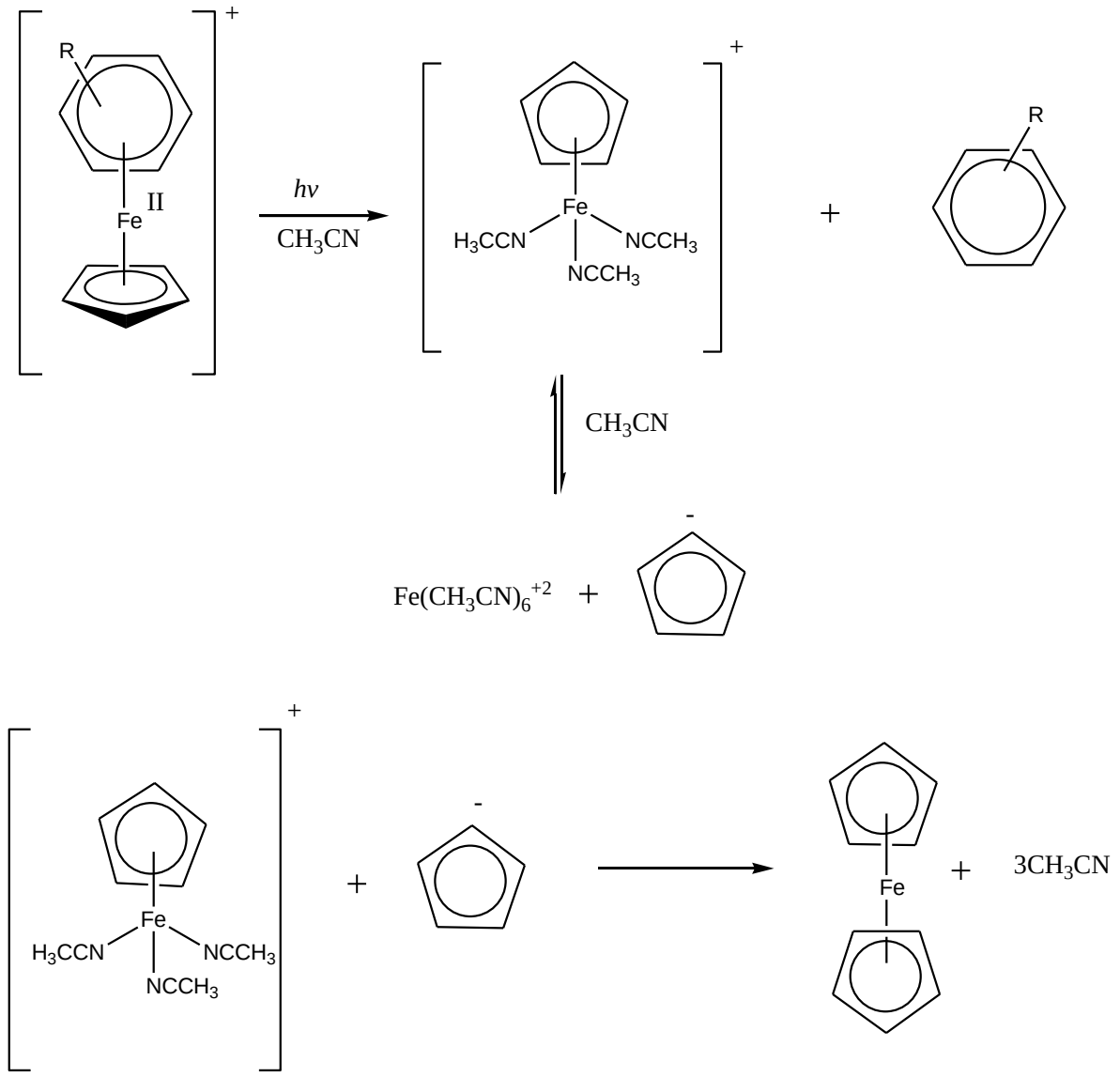


Scheme 1.07: The proposed mechanism of photolytic cleavage of the cationic cycolpentadienyliron moiety. X^- is a counter ion such as PF^-_6.



Scheme 1.08: Intermediate steps in photolytic decomplexation reaction.

1.3. Organometallic Polymers

1.3.1 Introduction

Organometallic polymers have been given much attention due to their promising catalytic, electrical, magnetic and optical properties. While many

materials contain metals within their backbone, others incorporate the metallic moieties pendent to the macromolecule. In many organometallic polymers, the moiety is an integral component of their structure, whereas in other situations, some metallic moieties are added to preformed polymers or may be removed from the polymeric material. Polymers with metal-carbon bond in their backbone contain hetero annular poly metallocenes transition metal-acetylides, and metal cyclopentadienes Figure 1.04 provides examples of some of the most common classes of organometallic polymers.[51-54]

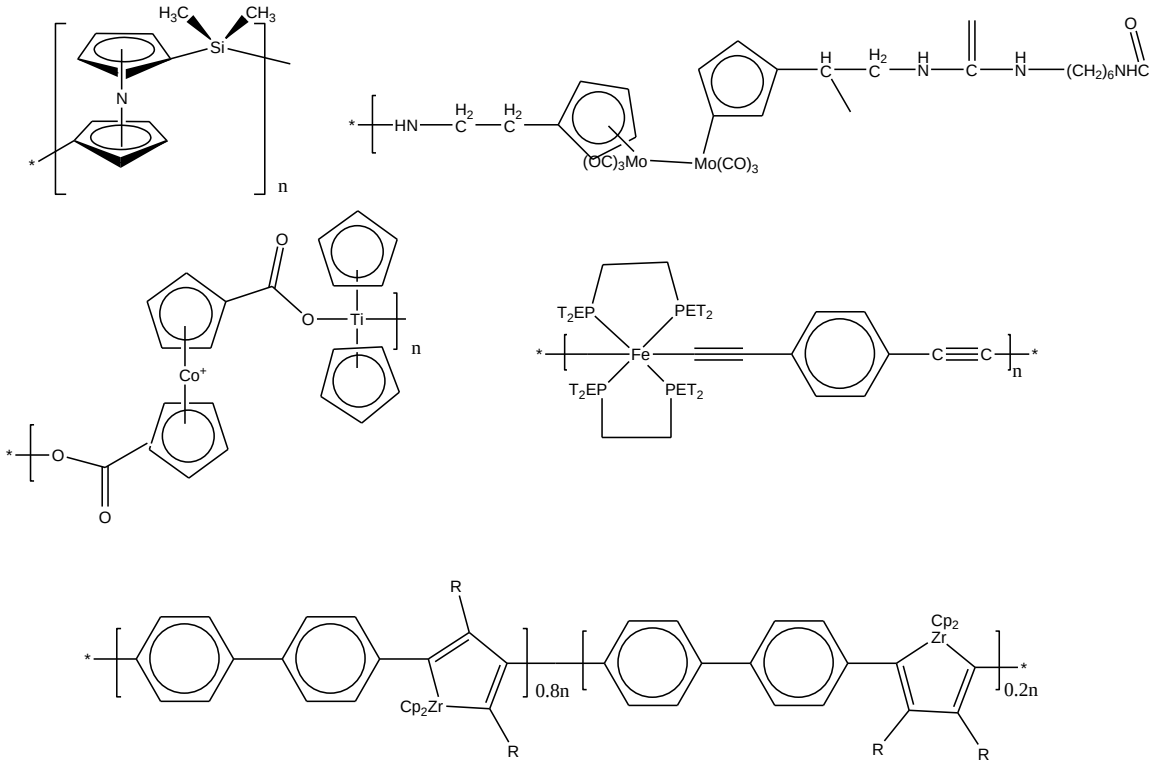


Figure 1.04: Polymers with skeletal metallic moieties

There are also many various classes of organometallic polymers in which the metallic moiety is pendent to the polymer backbone. Figure 1.05 provides an example of a polymer with pendent cyclopentadienyl cobalt moieties and a polymer with a tungsten group in the polymer side chains.

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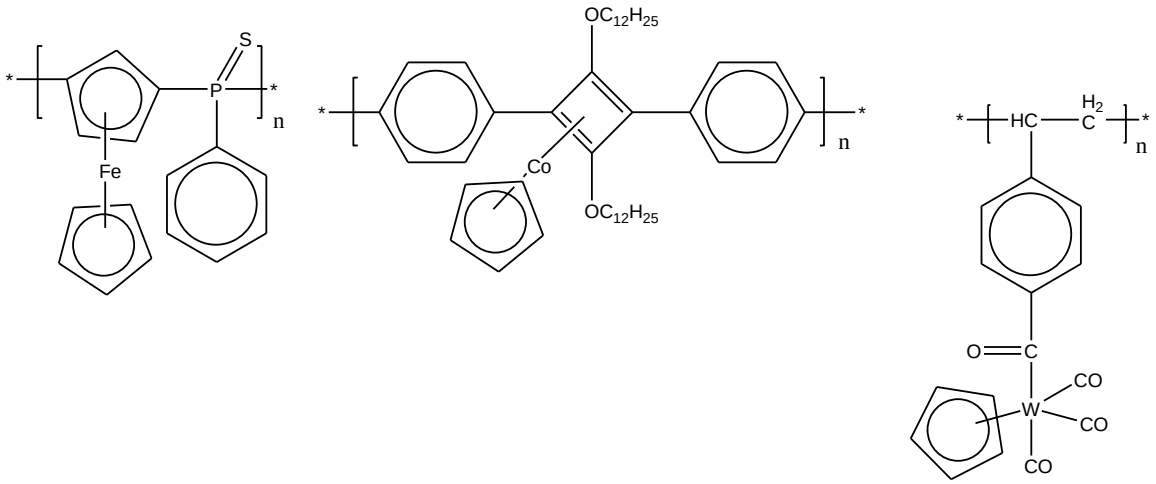


Figure 1.05: Polymers with pendent metallic moieties

1.3.2 Organometallic Polymers with Pendent Metal Moieties.

Polymers in which the metal moieties are incorporated to the backbone of a mostly organic polymer chain have a significant effect on the physical and chemical nature of the resulting materials. A universal disadvantage feature of all polymeric species, and one that continues to plague polymer chemists alike, is the decrease in solubility with the increase molecular weight. However, it

has been shown that a little difference in the polymer structure in the form of side group addition can enhance the solubility of the polymeric materials. A significant enhancement in polymer solubility has been noticed upon π-complexation of a metal moiety.[55]

The most easily applied procedure for the preparation of the metal including polymers was proposed in the 1960s with the invention of vinyl ferrocene and another vinyl transition metal–complexes undergoing polymerization under similar conditions as conventional manners to form the corresponding polymeric materials. [56] Vinyl-organometallic polymers are synthesized by the addition of the vinyl units where either X or Y or both could be metal-including moieties and result in with the preparation of homopolymers (when X=Y) or heteropolymers (when X≠Y)(See Figure 1.06).

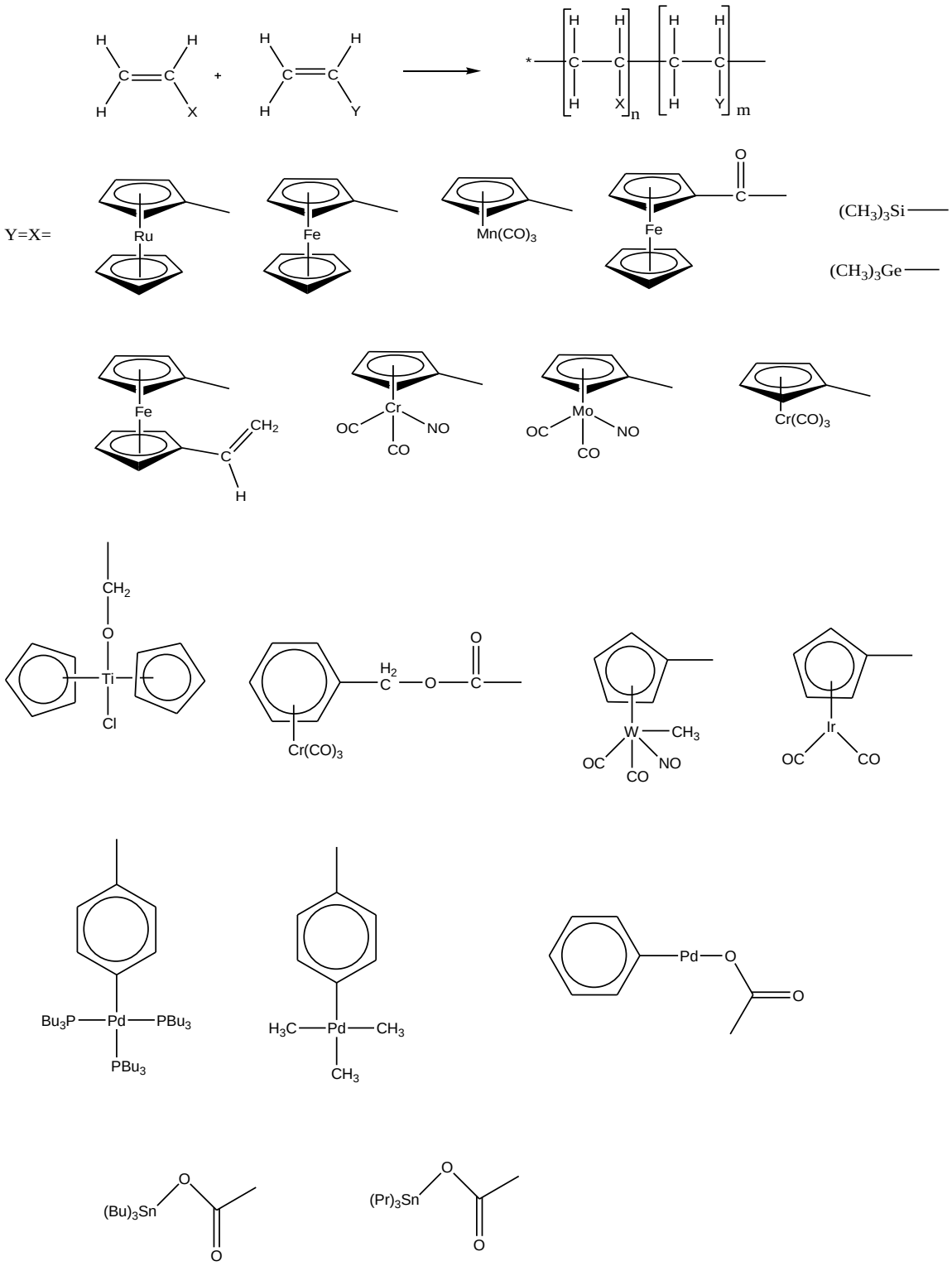
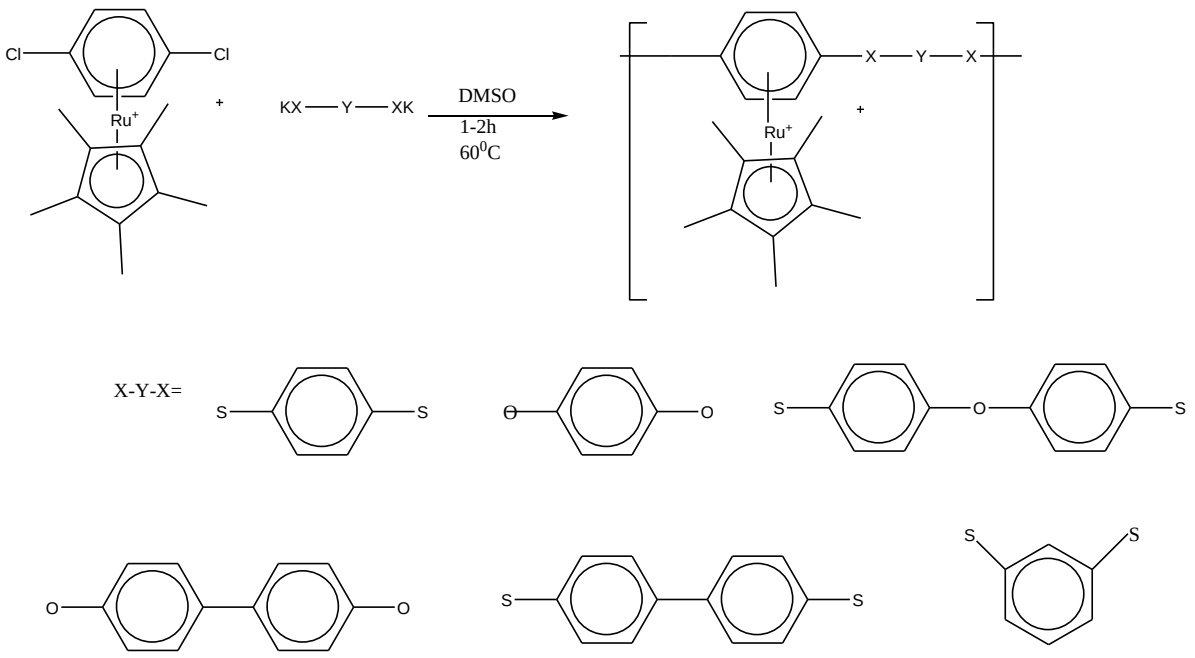


Figure 1.06: Structures of polymers with pendent metallic moieties from the addition of vinyl units.

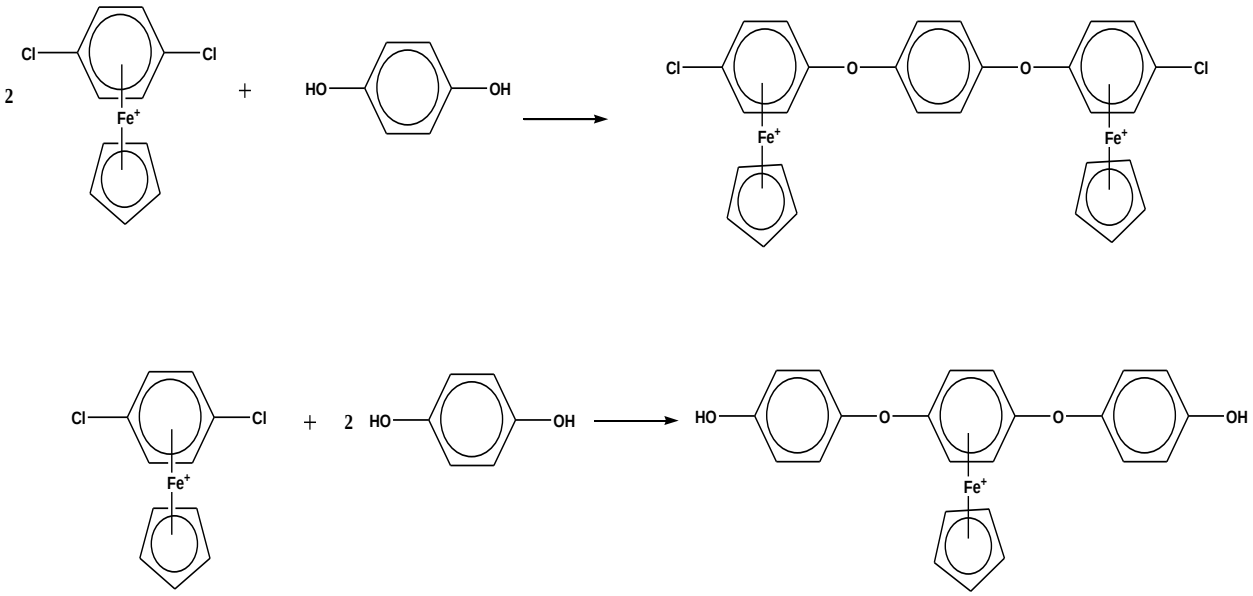
Figure 1.06 represents the variation of metals that could be added to the backbone of the polymer chain employing just one synthetic approach. It would be futile then to try a comprehensive study of polymeric materials of this type in any detail here. Thus, the subsequent investigation will be finite and contained to those studies in which the metallic species is incorporated to polymeric chains with etheric and thioetheric linkage. Recently, ruthenium has demonstrated considerable promise as the metal of choice in the preparation of polyaromatic ethers and thioethers with the incorporation of metallic moieties. In 1985, a remarkable communication by Segal showed the application of S_NAr reactions in the synthesis of poly (ether-ether-ketone) with pendent $CpRu^+$ metal moieties via photolytic demetallation or thermal arene replacement reactions, was a remarkable discovery for the synthesis of polyethers.[57]Due to the presence of the pendant metallic moieties, the solubility of the complex was improved in DMSO and acetonitrile relative to the insoluble nature of the purely organic analogue.



Scheme 1.09: The preparation of poly(phenylene sulfide) and poly(phenylene oxide) with pendent Cp^*Ru^+.

The preparation of the (1,4 dichlorobenzene)Ru^+Cp complex with the variety of aromatic ether and thioether dinucleophiles allows for the separation of the corresponding metallated polymeric materials.[55,58] Acetonitrile, DMF, and DMSO soluble metallated poly(phenylene sulfide) and poly(phenylene oxide) have been synthesized by Dembek and coworkers following the reaction sequence represented in Scheme 1.09. Despite Dembek's successfulness in the synthesis of metallated materials, there still needs to be research into separating the free organic polymers that are hindered by premature precipitation resulting in the incomplete elimination of the Ru^+Cp^* moiety.

Recently, Abd-El-Aziz and coworkers have illustrated the use of $CpFe^{+}$ activated chlorines in the stepwise synthesis of oligomer species with etheric linkages.[59] The procedure involves the consecutive reaction of *p*- dichloro and p-dihydroxy-terminated poly (cyclopentadienyliron) cations under very mild reaction conditions that allows for the synthesis of metallated oligomeric species with up to 35 pendent metallic moieties. Moreover, photolytic demetallation was successfully applied for the removal of the modified organic counterpart in which the molecular weight was virtually monodisperse. The synthetic strategy explained above is depicted in Scheme 1.10 and summarizes the controlled scheme of these oligomeric systems.



Scheme 1.10: Synthesis of starting materials for the stepwise synthesis of oligomeric polyethers with pendent $CpFe^{+}$ moieties

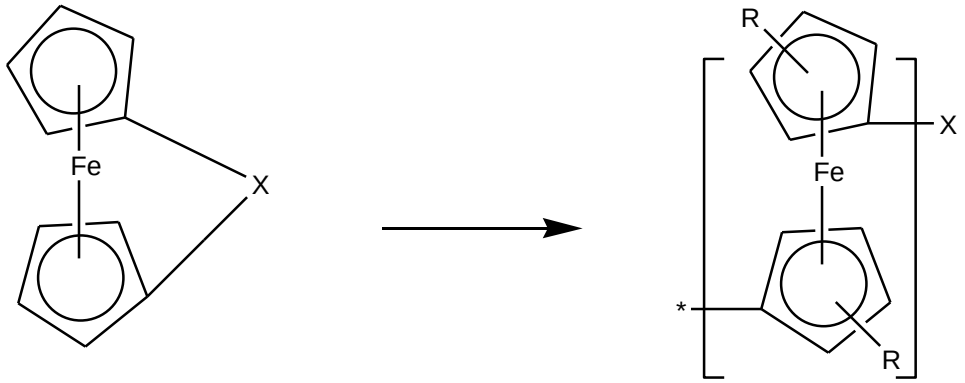
1.3.3 Polymers Including Metals in Backbone.

One of the goals of organometallic chemistry is to design stable, processable and high molecular weight polymers including metals as an integral part of the polymers. An effort has been made to enhance the polymeric properties of purely organic systems by the incorporation of various metal moieties into the polymer structures. [60-64] Coordination and metallocene polymers illustrate two examples of polymers that incorporate transition metal into the backbone of the polymer chain.

Currently, the main ways to synthesize metallocene including polymers is the condensation polymerization technique. The preparation of titanium-including polyester, polythioether and polyamines from the reaction of dicyclopentadienyl titanium dichloride (Cp_2TiCl_2) with diacid salts, diols, dithiols, and diamines are examples. [62] Similar examples of ferrocene-including polymers, as well as 1,1-ferrocenylenes, have been synthesized by a variety of coupling reactions. However, these procedures have resulted in the isolation of low molecular weight polymeric species.

The incorporation of ferrocene into polymeric structures has undergone resurgence due to the work of Ian Manners and his coworkers who have enhanced the use of ring-opening polymerization (ROP) as a new method for

the synthesis of polymers including skeletal ferrocene units. Ring opening polymerization happens via chain-growth process and demonstrates a unique way to the synthesis of metal-including polymers. The restrictive stoichiometric and conversion requirements, which often produce low molecular weight moieties via condensation technique, do not play a role here. [60] Manners has gained the advantage of beforehand-published studies of [1] ferrocenophanes, which demonstrated that these compounds have strained ring-tilted structures in which the planes of cyclopentadienyl ligands are tilted with respect to one another as compared to the parallel cyclopentadienyl ligands of ferrocene. [60,65] Scheme 1.11 represents the thermally induced ring opening polymerization of both [1] and [2] ferrocenophanes developed by Manners for the synthesis of ferrocene-including high molecular weight polymers. More recently, better control over the chain length of the desired species has been accomplished when [1] and [2] ferrocenophanes were exposed to ROP in the presence of an anionic initiator.[66-69]



X=SiRR,GeRR
PR,CH_2,CH_2

Scheme 1.11: Ring-opening Polymerization of [1] and [2] ferrocenophanes.

The incorporation of ferrocene into the backbone of the polymer chain has received much attention of the aerospace industry in studies of polymers with high thermal stability for utilization as lubricant and gaskets for jet engines, radiation shields and combustion regulators for solid-state rocket fuel.[63]Continued concern in these systems resulted from their intriguing electrochemical properties, which have exhibited proof for through bridge cooperation between the iron centers.[66,70-75]

Incorporation of transition metals into the backbone of the polymer chain is also investigated in the form of coordination polymers as a consequence of bridging of the metal by organic ligands.[63] Many transition metals, including the lanthanides and actinides, have been integrated into these types of metal-including polymers. The inclination of some of these materials to display a high degree of non-linear optical activity or electrical conductivity has motivated wide synthetic studies. The majority of these polymeric materials are not soluble, and in combination with their ease of degradation provide use for controlled release of drug or growth hormones. Figure 1.07 shows an example of a coordination polymer, which integrates ruthenium into the polymer backbone.[76]

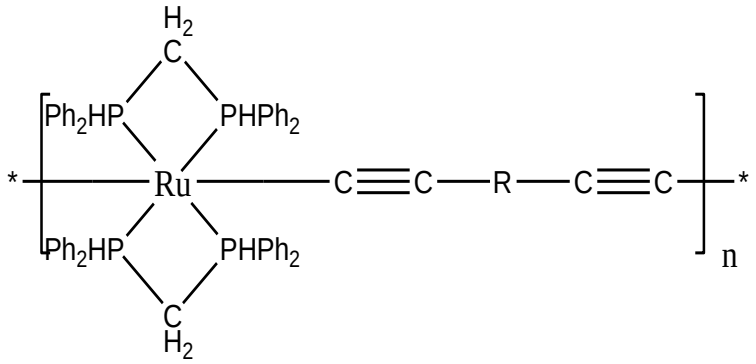


Figure 1.07: Ruthenium coordination polymers

1.4 Polyarylethers

1.4.1 Introduction

Polymeric materials, which incorporate aryl ether linkages as an integral component of their molecular structure, have fundamental characteristics such as thermal stability, chemical resistance, flame retardancy, high mechanical strength and potential electrical properties.[77-84]These attributes contribute the basis for a family of polymeric materials known as "high-performance plastic" or "engineering plastic". The commercial improvements of these materials have produced a class of high-performance plastics that are identified by their superior performance in some desirable applications. [77,79,85-87] Engineering plastic frequently participates in industrial markets formerly dominated by metals and high potential exists for enhancing the development of these materials with far-reaching consequence.

The interest in the commercial improvement of engineering plastic arises from a balance of their properties as well as their cost efficiency. [86] The advantage of these materials is magnified by the integration of different chemical functionalities into the polymer structure in an attempt to produce specific qualities. [82,83,86,88,89] Several industrially notable high-performance engineering thermoplastics are illustrated in Figure 1.08 and combine ether,

thioether, carbonyl, sulfone, and amine linkages within the backbone of the polymer chains.

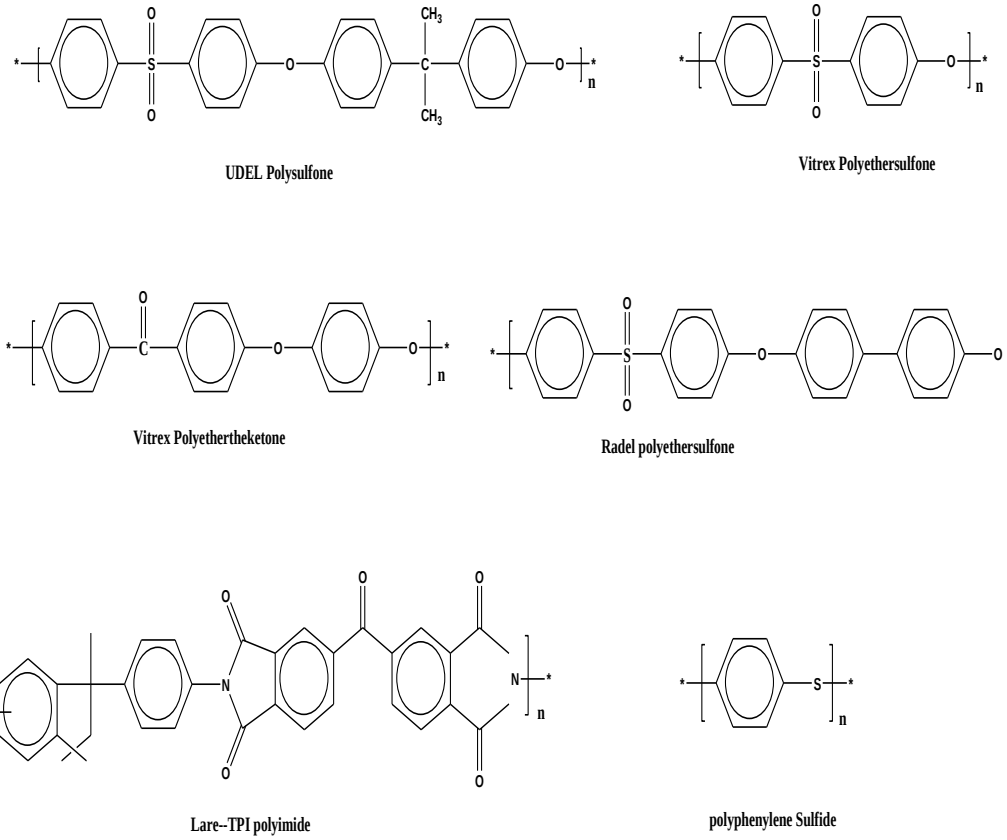
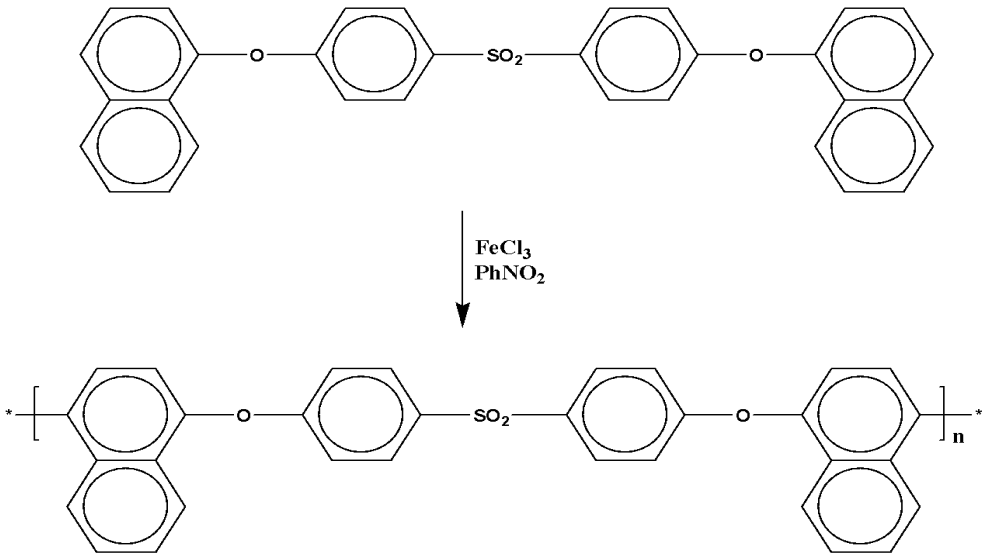


Figure1.08: Industrially important engineering thermoplastic.

Because of structural difference in these materials, none of the synthetic approaches have been improved for the synthesis of the above polymers. Thus, the synthetic procedure applied for polymer synthesis is selective with respect to the structural complexities of the material itself and its proposed purpose.[88,90]

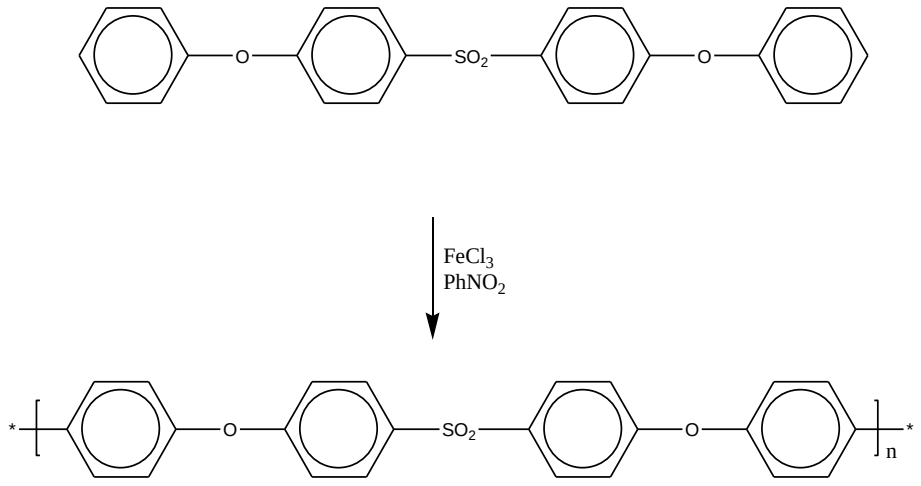
1.4.2 Scholl Reaction

In the last few decades, Percec and coworkers have shown the use of the Scholl reaction in the synthesis the different polyethers. Essentially, the Scholl reaction involve the elimination of two aryl ether hydrogen atoms forming an aryl-aryl bond in the presence of Friedal-Craft catalysts. [91-98] Extensive study has demonstrated that the reaction proceeds most successfully when dinaphthoxy contain monomers undergo polymerization in the presence of ferric chloride as a catalyst. The polymerization takes place in nitrobenzene at room temperature. Scheme 1.12 illustrates an example of the Scholl reaction for the synthesis of a polyethersulfone.



Scheme 1.12: Synthesis of a polyethersulfone via the Scholl reaction

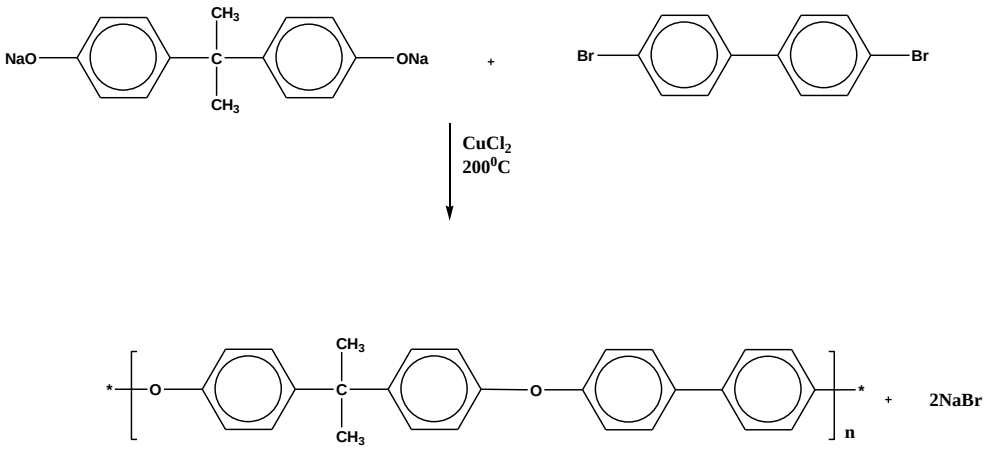
The reaction is assumed to take place via a cationic-radical mechanism where $FeCl_3$ produces a radical-cation at one of the naphthoxy groups because of the one-electron oxidation of the monomer. [94,96-98] It is the ease of oxidization of the naphoxy groups in this initial step that causes these monomers to easily undergo Scholl polymerization. Chain growth contains continues due to either electrophilic or radical propagation steps with termination eventually occurring due to the combination of the cation-radical with a counter-anion or with a fragment of it. While several attempts have been made to synthesize some commercial poly aryl ethers by the reaction of biphenyl terminated monomers as exemplified in Scheme 1.13, only low molecular weight materials were obtained.[84, 86-88]



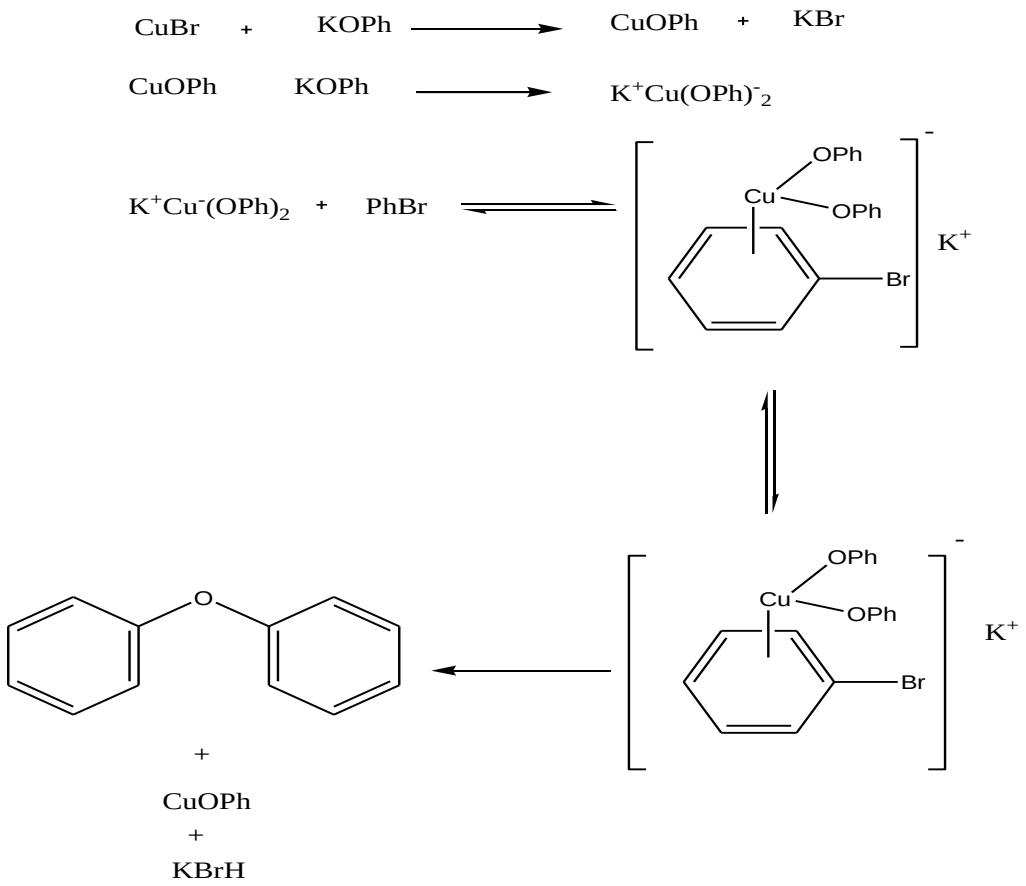
Scheme 1.13: Low molecular weight polyethers with diphenyl terminated monomers.

1.4. 3 Ullman Polymerization

The investigations of Ullman in the early 1900s regarding the synthesis of diaryl ether expedited the development of the well-known nucleophilic and electrophilic process, which has been used in the commercial preparation of many engineering thermoplastics. The Ullmann reaction is the most useful method to prepare polyaromatic ethers, and consist of the reaction of alkali metal phenoxides with aryl halides where an electron-withdrawing group does not activate the halogen in the electron-withdrawing group. [80,99] Scheme 1.14 represents the reaction of the sodium salt of bis-phenol A with dibromo monomers under Ullmann reaction conditions. Copper based species such as copper halides, copper oxides, and metallic copper have been utilized as catalysts in the reaction. [100] From mechanistic investigation it was deduced that the cuprous ion is the active species which coordinate with the π-system of aromatic halides creating the resulting complex which is more susceptible to carbon-halogen cleavage (Scheme 1.15). [101-103]



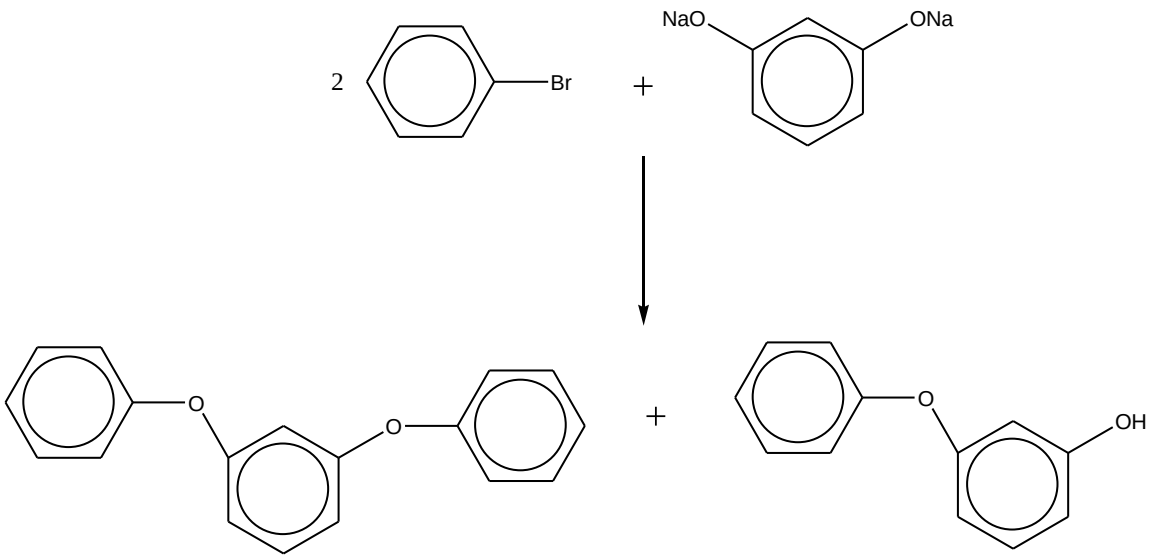
Scheme 1.14: Synthesis of poly (1,4-phenylene oxide) using Ullman reaction conditions.



Scheme 1.15: Mechanism of the Ullmann reaction

Several features of the reaction conditions have been recognized as playing influential roles in determining the success of this process. For example, the phenols usually reacted in the presence of their corresponding alkali metals salts displayed greater reactivity with potassium peroxide over the sodium counterparts.[99] An interesting observation of this reaction is the ease of halide replacement with respect to the haloaromatic monomer. The activity of aryl halide is considered to be reverse of that seen for polyether formation from activated halides or in short decrease in the order I>Br>Cl>F.[100-105]The impact of the aromatic halide is most clearly demonstrated by the significant drop in yield, from 70% to 10%, experienced in using iodobenzene or chlorobenzene, respectively, under the same reaction conditions. Despite the high yields of product separated with the use of iodobenzene reactants, the expense of these compounds often supports the use of their brominated derivatives with a slight decrease in yield. In addition to these studies of the haloaromatic reactants, the activity of the phenolic unit was completely hindered by the presence of methyl group in both ortho positions. On the other hand, the presence of one ring substituent ortho to the hydroxyl group was not shown to affect the yield of the reaction significantly.[104]

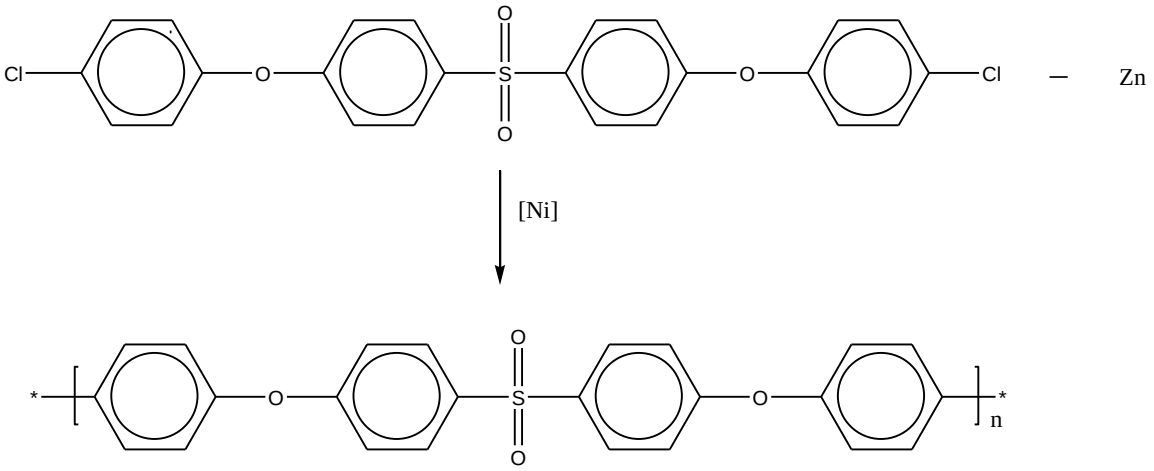
Another view of the reaction factors that has been demonstrated to be influential in the success of product formation is the choice of the solvent. Even though various solvents such as DMF, HMPA, DMSO, collidine, pyridine, and nitrobenzene are potential solvents for the Ullmann reaction, cuprous chloride in pyridine has been noted to be the preferred catalyst/solvent system. [105] Scheme 1.16 represented the reaction of the sodium salt of 1,3-dihydroxybenzene with bromobenzene forming the separation of two products, 1,3-dihydroxybenezne and 1,3 phenoxyphenol. Concerning the reported solvent studies, of particular interest is the significant effect that water and acidic solvents had on the efficiency of the reaction. Even though the above reaction takes place in pyridine resulting in the isolation of 1,3 diphenoxybenzene and 1,3 phenylphenol in 72% and 15% yields, respectively, the addition amount of water (2%) resulted in a decrease in the yield to 22% and 4%. Even though the Ullmann ether synthesis has been noted as a viable route to the synthesis of polyethers, its potential for industrial application is hindered by possible side reactions such as the Ullmann coupling process reductive dehalogenation and halogen exchange between the catalyst and aryl halides.



Scheme 1.16: two products forming from the Ullman reaction in the presence of acidic solvents.

1.4.4 Nickel-Catalyzed Coupling Reaction.

Nickel-catalyzed coupling demonstrates one of the most useful methods to synthesize polyethers. The reaction of dihalides (Scheme 1.17) takes place in the presence of zero-valent nickel, which helps the formation of an aryl-aryl bond by the elimination of two aryl halides.[106,107110]The polymerization occurs most effectively under an inert atmosphere in a dry aprotic solvent in which zero-valent nickel is created from a three-component mixture of nickel salt, triphenylphosphine and metal such as Mg, Mn or Zn.[107]

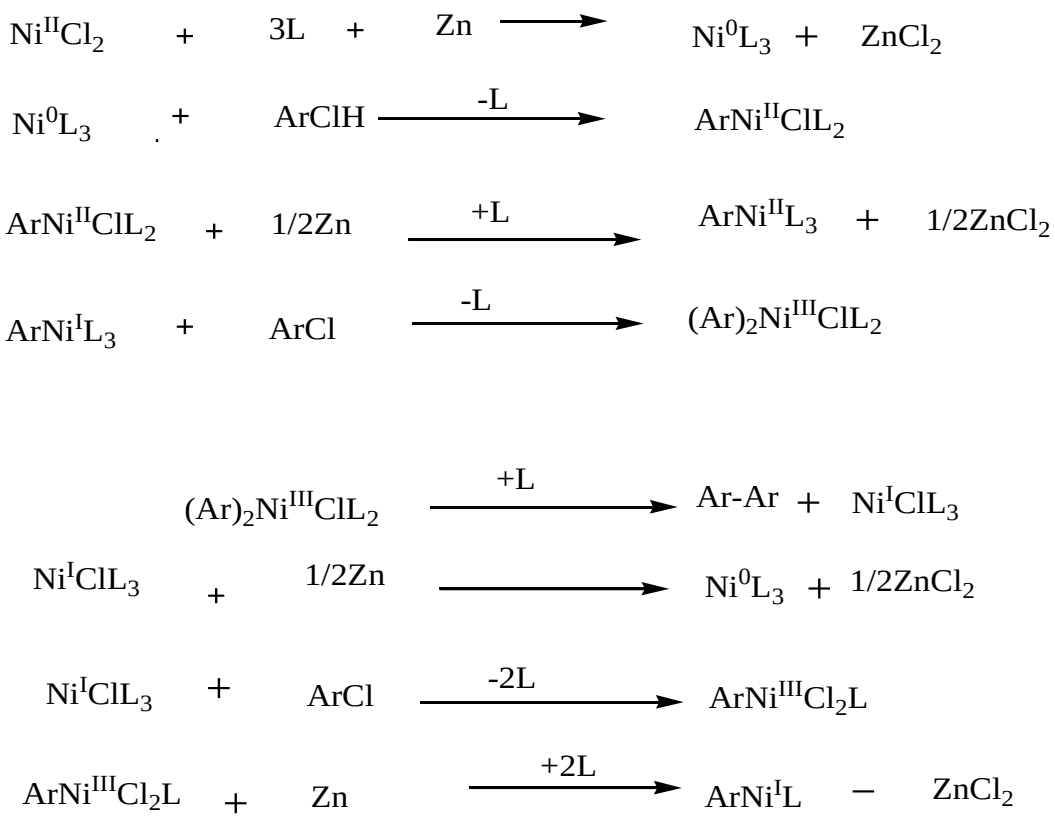


Scheme 1.17: Nickel catalyzed synthesis of a polyethersulfone.

More specifically, optimal reagent mixtures are made up of a less than 2% molar ratio of nickel respective to the amount of aryl dichloride, high triphenylphosphine/nickel ratios and an excess of zinc, which is subjected to moderate reaction temperature. Moreover, units must be selected carefully to ensure those functional groups present are inert toward the zinc/nickel catalyst system. It has been noticed that electron-withdrawing substituents allow for the isolation of the products in the greatest yield with the exception of nitro and aprotic groups, which are not tolerated at all. [106,107]

Scheme1.18 describes the suggested mechanism of the nickel-catalyzed

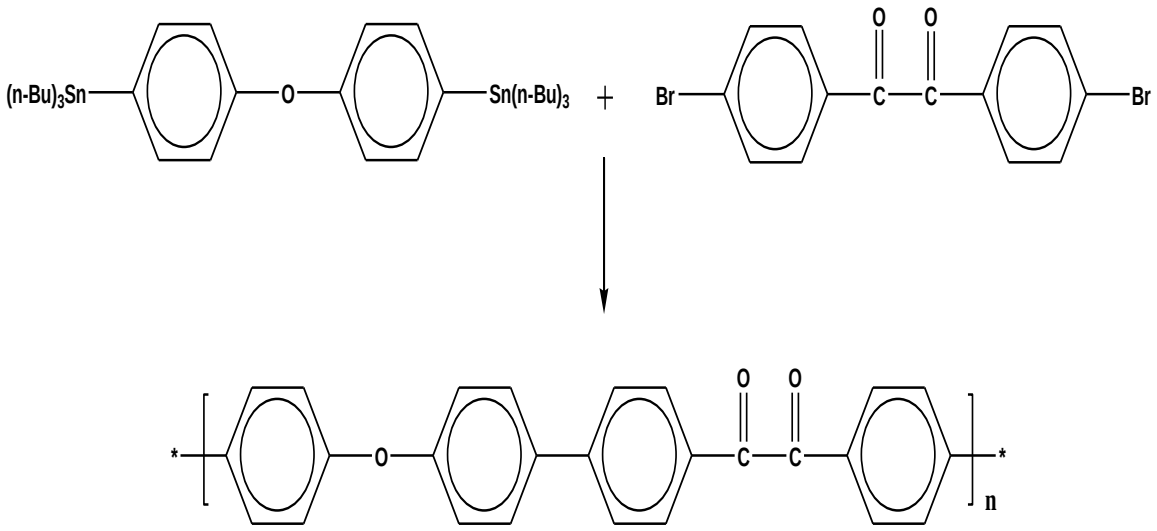
polymerization process. It is assumed that the first step in the process requires the formation of the active zero valent complex by the reduction of the nickel halide nickel(II) to nickel(I). The following oxidative addition of the aryl chloride results in the generation of the corresponding nickel(II) intermediate which, following a reduction in the presence of zinc, experiences a second oxidative addition of aryl chloride in the production of a diaryl nickel complex. Liberation of the diaryl product requires an active reductive elimination process yielding a nickel(I) complex which is reduced further and may re-enter the cycle. Meanwhile, a nickel(I) species could react with aryl chloride by oxidative addition to produce an aryl nickel(III) intermediate, which is reduced to aryl nickel and may re-enter the cycle in this form.



Scheme 1.18:The nickel catalyzed mechanism

1.4.5 Palladium-Catalyzed Cross-Coupling of Tin Reagent.

The coupling reaction of bifunctional tin reagents with dihalides in the presence of a palladium catalyst has been established as an effective route to polyether. Scheme 1.19 is an example of the polymerization of 4,4-bis (tributylstannyl) diphenyl ether with 4,4-dibromodiphenyl sulfone to yield moderately high molecular weight polysulfide.



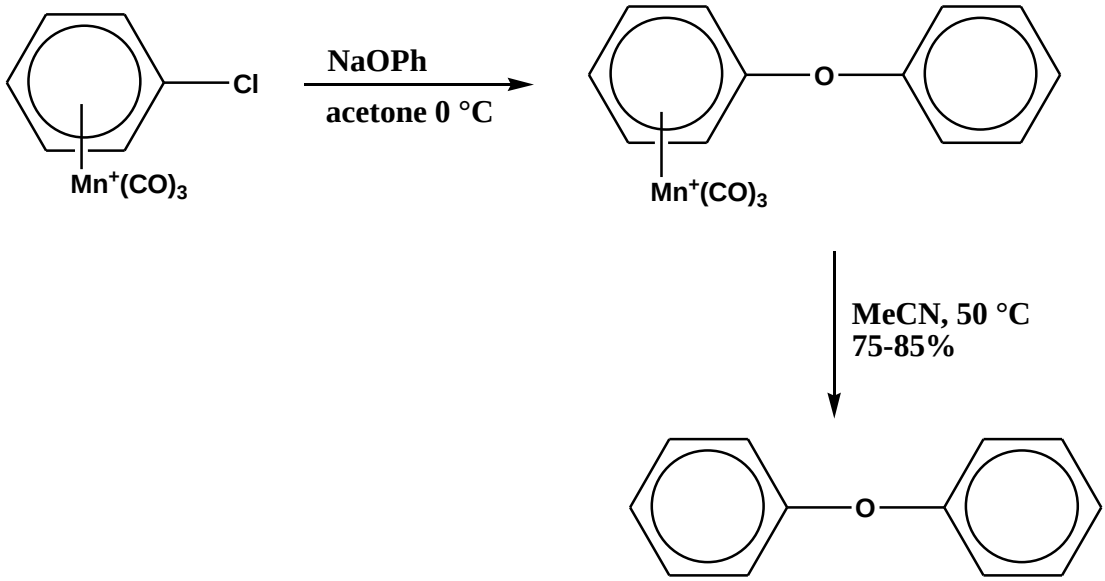
Scheme 1.19: Palladium catalyzed polymerization of 4,4' -bis (tri-n-butylstanny 1) dipheny1 ether with 4,4'-dibromodiphenyl sulfone.

A 2:1 triphenylphosphine:palladium chloride catalyst system in dimethylacetamide (DMA) at 165°C has been proven as the perfect condition for the reaction. However, as is the case with most synthetic technique, there are both advantages and disadvantage to utilizing this procedure. This procedure takes advantage of pendent functional groups, which may be contained in the monomers units from low reaction yields.[108,109]

1.4.6 Temporary Complexation to Metal Moiety.

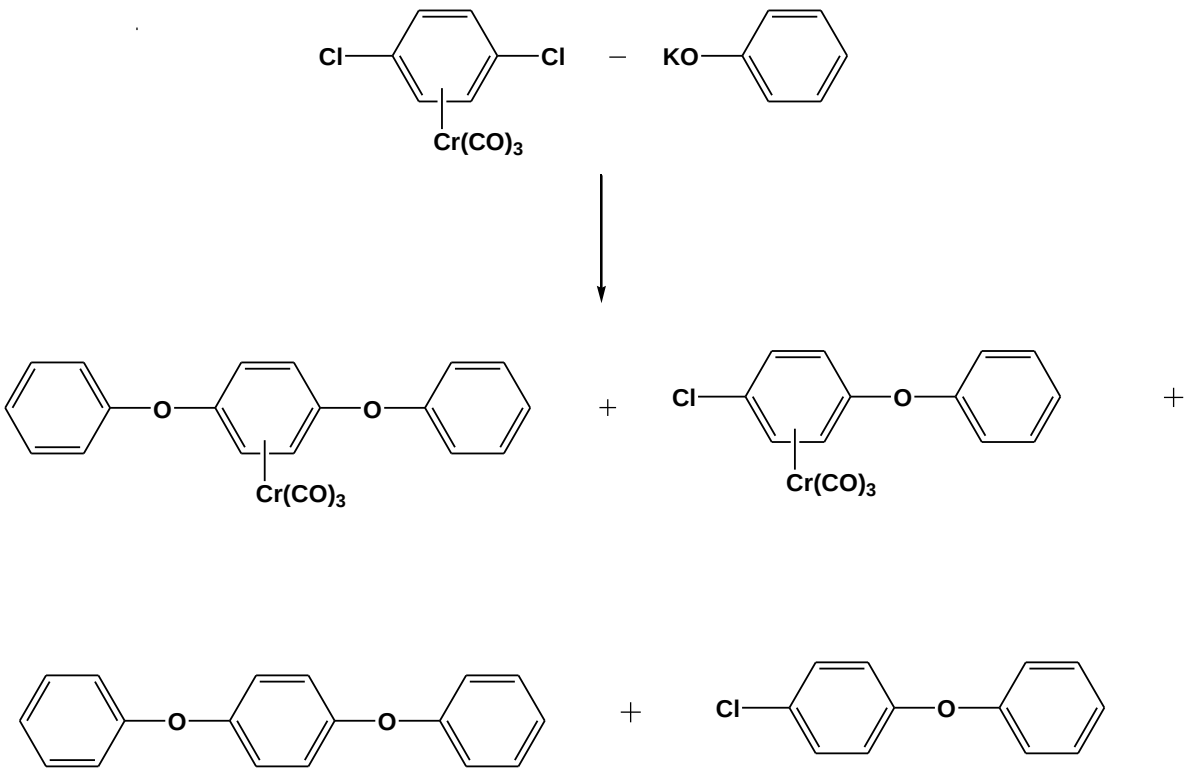
The activation of chlorines toward nucleophilic aromatic substitution reactions upon complexation to a metal moiety has been investigated as a potential alternative in the preparation of polyethers and thioethers.

Based on the excellent reactivity of $(CO)_3Mn^+$ complexed chloroarenes toward reactivity with different nucleophiles, it is no wonder that these complexes have been studied as possible routes to ether preparations. [110-112] Scheme 1.20 shows the reaction of a $(CO)_3Mn^+$ complex with the sodium salt of phenol in the synthesis of the corresponding diphenyl ether. Pearson utilized this procedure in the synthesis of a variety of diethyl ether and triaryl diethers, and may be utilized further as a precursor in natural product syntheses. Despite the success experienced in using the complexation of this metallic moiety for the incorporation of etheric linkages, the inability to prepare 1,2 , 1,3 and 1,4 dichloroarene complexes restricts further use of this process for this polymer synthesis.[112]



Scheme 1.20: Complexation of the $(CO)_3Mn^+$ in the promotion of chloroarene towards S_NAr reactions in the synthesis of ether linkage.

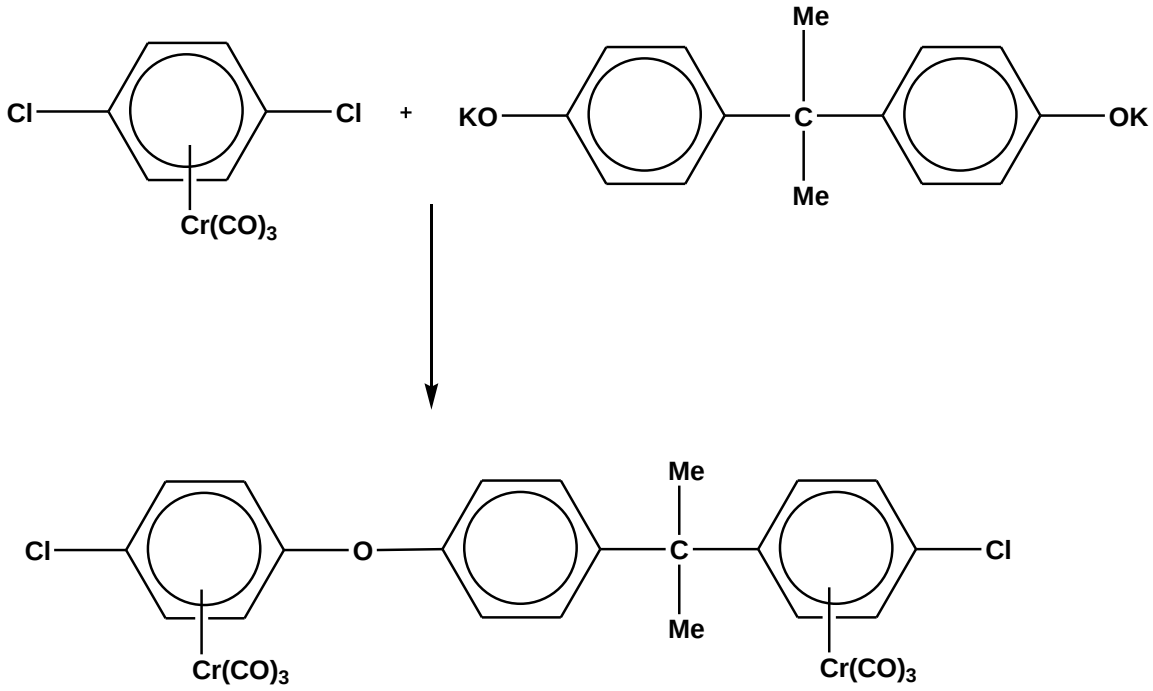
It was stated previously that in comparison to other metal moieties that have been utilized to activate haloarene towards nucleophilic aromatic substitution, the $Cr(CO)_3$ complexes have been proven to have the least reactivity. The reaction of (1,4dichlorobenzene)-$Cr(CO)_3$ with mono-or-diphenoxide, has ended up in the synthesis of aryl ether. [113,114] The drawback of this reaction was the inability to obtain the desired disubstituted product without having to isolate it from the mixture of the products that causes the reaction seen in Scheme 1.21**.**



Scheme 1.21: Nucleophilic aromatic substitution of (1,4- dichlorobenzene) Cr $(CO)_3$ with the potassium salt of phenol.

Double nucleophilic substitution of (1,4 dichlorobenzene)-Cr $(CO)_3$ with potassium salt of bisphenol A was also successfully accomplished and display the potential for the creation of high molecular weight species via further nucleophilic substitution. The effectiveness of this reaction in the presence of 18-Crown-6 with a reaction time of 2 hours is demonstrated by the isolation of the desired product in 73% yield (Scheme 1.22). The reduced reactivity of $Cr(CO_3)$ complexes requires the use of a polar aprotic solvents, high

temperatures, prolonged reactions times, and phase transfer catalysts such as 18-Crown-6.



Scheme 1.22: Double nucleophilic substitution reaction forming from the synthesis of bimetallic Cr $(CO)_3$ complexes.

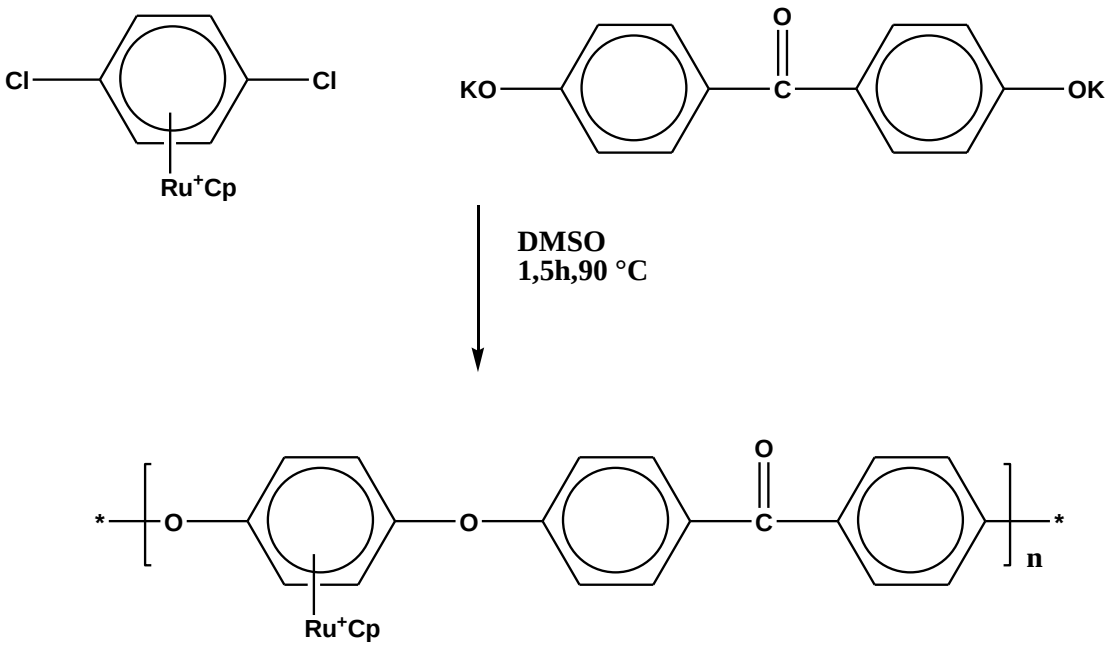
Recently, ruthenium and iron-based metal moieties have gained much attention as possible route to ether and thioether containing compounds. The limited activation capabilities are comparable to the chromium and manganese metal moieties in addition to the number of chloroarenes to which they can form complexes. The simplicity of liberation of their modified ligands from the complexes and environmentally safe-co-ligands are two of the attractive qualities of iron and ruthenium complexes. Several studies have outlined the

utilization of $CpRu^+$, Cp*Ru and $CpFe^+$(chlorine) metal complexes for the incoporation of aliphatic and/or aromatic ether and thioether linkages in various compounds.

In particular, two various methods have been studied in the use of $CpFe^+$ and CpRu complexes as an alternative route to the synthesis of thermally stable engineering plastic. The first approach benefits from the ease with which modified organic ligands may be isolated from their corresponding organometallic counterparts. This has allowed for the synthesis of unique organic monomeric units, which are useful for polyesterification or the Scholl procedure in the preparation of polymers. For instance, Pearson and coworkers have utilized the polyesterification of monomers created utilizing these organometallic methods to synthesize poly (ether-ester).[115-117]

Segal began the introductory investigation in connection with the nucleophilic aromatic substitution ability of pendent metallic moieties in the synthesis of organometallic polymers. [57] He successfully synthesized high molecular weight poly (ether-ether-ketone) with pendent $CpRu^+$ moieties as seen in Scheme 1.23.[57]Moreover, Segal was capable of isolating the organic polymers species easily by photochemical or thermal arene displacement. Unfortunately, the organometallic poly(phenylene oxide) and poly(phenylene

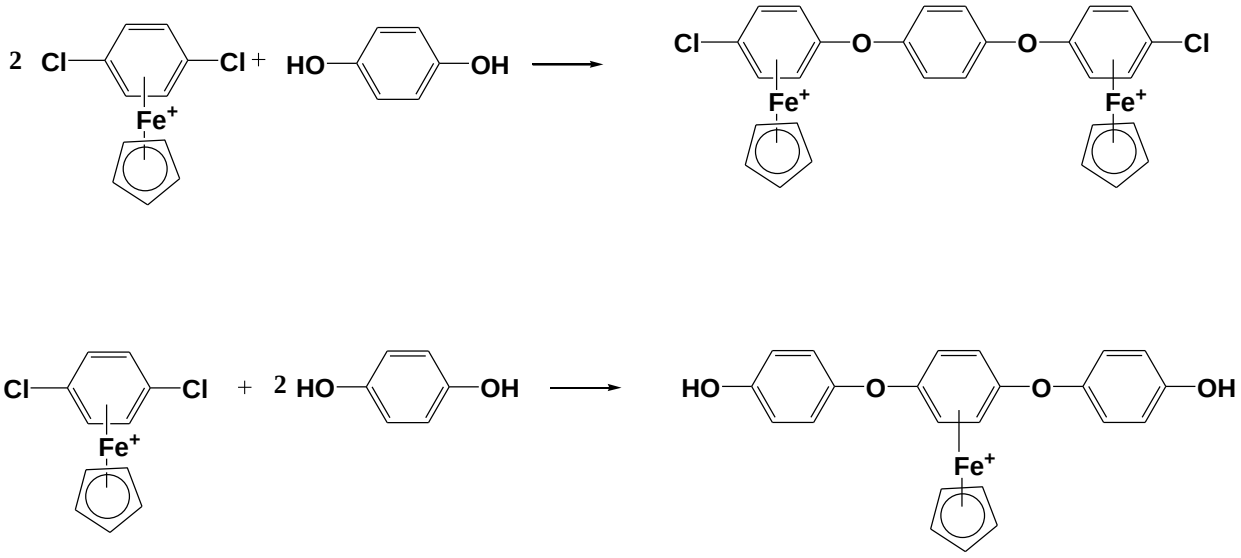
sulfide) materials generated by Dembek and coworkers by the reaction of (1,4 dichlorobenzene) Cp*Ru^{+} with different dihydroxy and diethoxy-aromatic nucleophiles were not able to be isolated as their organic counterparts as shown in scheme 1.09. [58,118,119]



Scheme 1.23 : The synthesis of poly(ether-ether-ketone) with pendent CpRu* metal moieties.

Until recently, the use of the ligand exchange reaction of a polyaromatic compound with excess ferrocene was the main approach for producing high molecular weight species with pendent $CpFe^{+}$ moieties.[41,120-123] The nucleophilic aromatic substitution of a 2:1 molar ratio of mono-or dichloroarene $CpFe^{+}$ complexes with aliphatic or aromatic diols has enabled the separation of various diiron complexes.[36,57,124,125] Extensive study of this technique using

aromatic diols has determined that employing either a one- or two-step reaction strategy provides the chance to prepare symmetric and asymmetric species, respectively. An expansion of this procedure has been utilized to synthesize the oligomeric aromatic ether having up to 35 cationic metals (Cp)Fe^{+}.[125] The general route strategy for this synthetic approach is based on the structure of monomers generated from the reaction of (1,4dichlorobenzene) Fe^{+}Cp hexafluorophosphate and hydroquinone and is schematically illustrated in Scheme 1.24.



Scheme 1.24: Synthesis of reactant materials for the stepwise design of oligomeric polyethers with pendent $CpFe^{+}$ moieties.

Primarily, the chain length of oligomeric species experiences an increase via consecutive nucleophilic aromatic substitution reactions of chloro-and-hydroxy-terminated metallic species. The use of a 2:1 molar ratio of a complex including two terminal hydroxy substituents with (1,4dichlorobenzene) .$Fe^{+}Cp$ allowed for disubstitution of the chlorine substitutions and resulted in the isolation of high molecular weight species with terminal hydroxyl group. Alternatively, the reaction of a dichloro-terminated oligomeric species with hydroquinone in a 2:1 ratio resulted in dichloro-terminated complex with the expected number of metallic moieties. The consecutive reaction of the terminal dihydroxy with dichloro substituents of the resulting oligomer polymetallic product allows for control over the nature and molecular weight of the resulting product. This procedure has been shown to be a unique strategy in the synthesis of polyaromatic ether.

This synthetic scheme illustrates an effective alternative to aromatic ether synthesis under very mild reaction conditions. Photolytic demetallation of the organometallic oligomer isolates the pure organic analogue in excellent yield.[36,124,125]The disadvantage of this synthetic strategy is the numerous reaction steps, which have to be employed to obtain high molecular weight species. An apparent advantage of this methodology over conventional

approaches is the ability to control the molecular weight of the resulting species specifically.

1.5 Surfactant Behaviour

1.5.1 Introduction

Surfactants are a significant class of chemicals with two moieties that behave differently upon contact with a solvent, [126-129-]with water usually considered as the solvent of interest. The word amphiphiles comes from Greek roots.[129] First, the prefix amphi which expresses double, " from both side" ,"around". After that, the root philos means friendships or affinity, as in "hydrophilic" (compatible with water). Thus, an amphiphilic substance exhibits a double affinity. One moiety, the hydrophilic head of the surfactant, contacts satisfactorily with the solvent. The other moiety, the hydrophobic tail, contacts unfavourably with the solvent. The term surfactant is a contraction of the phase surface-active agent. Surfactant molecules are present in everyday life playing an essential role in many fields such as detergents, food, paint, pharmaceutical products, cosmetics and industrial and biological processes. [127,129,130] Symbolically, a surfactant molecule can be illustrated as consisting of a polar head and a non-polar tail as represented in Figure1.09.

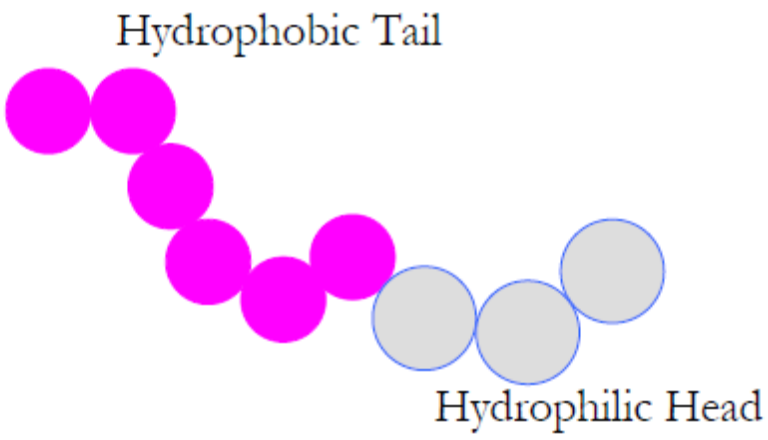


Figure 1.09: Illustration of the hydrophilic and hydrophobic portions of an amphiphilic molecule.

The dual amphiphilic nature of surfactant towards water leads to the segregation of hydrophobic tails from the water. Furthermore, the exposure of the hydrophilic heads to water results in two interesting and useful phenomena in aqueous solution: their preferential adsorption at interfaces (e.g. oil/water) and at the surface (e.g. air/water) they may form a variety of microstructures, known as micelles, as shown in Figure1.10.[126,127,129-132]

The polar (hydrophilic heads) group of the surfactants can be charged or uncharged and may contain heteroatoms such as O, S, P or N; present as acid, sulfate, sulfonate, phosphate, amine, amide, etc. The apolar group is usually a saturated or partially unsaturated aliphatic chain. The hydrophobic group in a surfactant for in use in an aqueous medium is usually a hydrocarbon chain (-

CH_2-) but could also be fluorocarbon or siloxane (R_2SiO) appreciable chain length. In addition, aromatic groups, such as benzene rings may be present in the surfactant tail. The polar portion is also known as the hydrophilic part or hydrophile. The apolar part is called hydrophobic or lipophile, from Greek roots phobos (fear) and lipos (grease). The unusual properties of aqueous surfactant solutions can be attributed to the presence of a hydrophilic head group and hydrophobic tail group in the molecule. The presence of these types of molecules in aqueous solutions has an intense effect on the properties of interfaces and surfaces. Apart from interfacial effects, the presence of surfactant in the aqueous phase represents a wide range of phase behavior of which the formation of micelles or bilayers are well known example.

Since surfactant molecules possess hydrophilic and hydrophobic parts, the desirable location for them in water are at the surface where the forces of both attraction and repulsion to water can be fulfilled. Surfactant molecules aggregate in water above a threshold concentration, creating micelles to reduce the contact of the hydrophobic groups of the surfactant with water. Two facts cause the spontaneous formation of micelles. First of all, the hydrophobic effect creates the nonpolar portion of the molecule to be isolated from water and separated in the interior of the structure. Second, interaction between the head of the group determines how closely the molecules may be packed. The

self-assembly of the surfactant molecules in water into spherical micelles is shown schematically in Figure1.10. A micelle consists of hydrophobic tails in contact with one another. The hydrophilic regions where the heads of the surfactant molecules contact with water surround these hydrophobic areas. Micelles produce various geometric shapes, including spheres, cylinders, disks, etc., and always in a manner that minimizes the contact of the hydrophobic tails with water while maintaining the desirable contact of the hydrophilic heads with water.

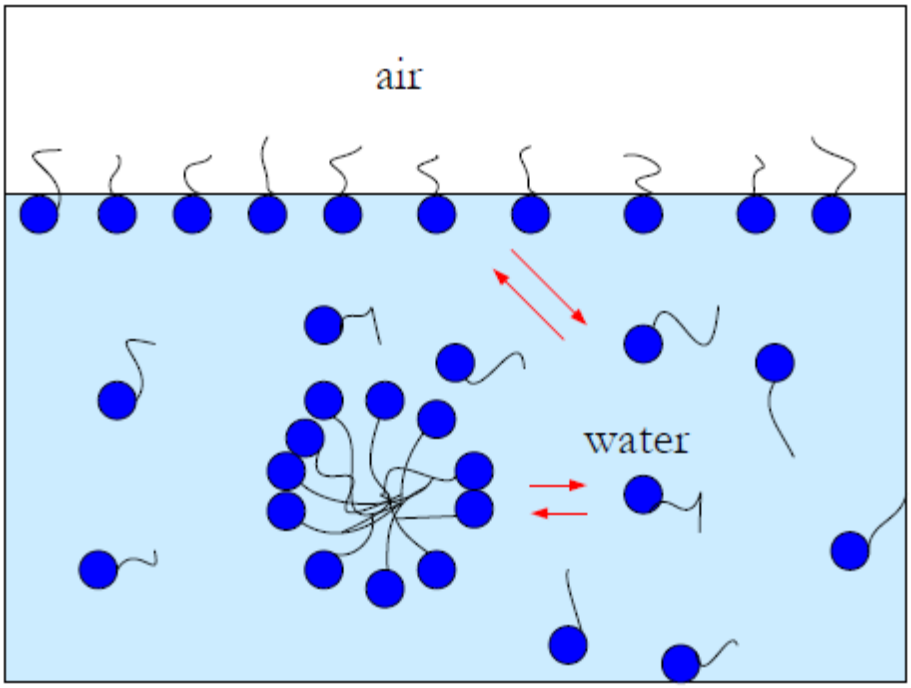


Figure 1.10: Aggregation and orientation of surfactants, to minimize the hydrophobic tail-water connection.

At low concentrations, surfactants form a dilute homogeneous solution of individual molecules, while at high concentrations, above a threshold concentration, the amphiphilic molecules self-assemble into aggregates or microstructures identified as micelles. These micelles coexist with singly dispersed surfactant molecules know as free surfactants in the bulk solution. The surfactant molecules contained in the micelle have their hydrophobic tails protected from water in the aggregate interior, the core of the micelle, and their hydrophilic heads exposed to water at the aggregate surface, the micelle core-water interface referred as the corona.

1.5.2 Type of Surfactants:

Surfactants can be divided according to their physical properties or functionalities. The following is the most well known categorization, and it is depend on the nature of the hydrophilic groups: [126,127,131,133]

1-Anionic Surfactants: the hydrophilic group of the surfactant molecule carries a negative charge, for example, $RCOO^- Na^+$ (soap or carboxylic acid salts) $RC_6H_6SO^-_3 Na^+$) (alkylbenzene sulfonate).

2-Cationic Surfactants have positively charge hydrophilic groups. For instance, RNH^+_3 (salt of long chain amine), $RN(CH_3)^+Cl^-$ (quaternary ammonium chloride).

3- Zwitterionic: both positive and negative charge could be displayed in the hydrophilic groups, for instance, $RN^{+}H_2$ (CH_2) COO^{-}, (long-chain amino acid), sulfone, $RN^{+}H_2$ (CH_3) CH_2CH_2 $SO^{-}_{3.}$

1.5.3 Applications of Micelles.

Micelles have many advantages that can be utilized for drug delivery, detection and mapping of primary cancer and distant metastases, and as a platform for therapeutic applications. Namely, micelles can: 1) increase the water solubility of many cancer agents; 2) demonstrate prolonged circulation kinetics; 3) assist in enhancing accumulation of agents (therapeutic or diagnostic) at tumour sites through the enhanced permeability and retention (EPR) effect; 4) be tailored to a specific size (i.e. 10-100nm) to help enhance extravasation and penetration in tumour tissue, as well as localization in specific subcellular compartments (i.e. nucleus); 5) deliver a large therapeutic/diagnostic load; 6) be changed to target any particular cell type or intracellular compartment and thus may be helpful for treatment of a wide number of cancer types, and 7) be synthesized from entirely biocompatible and/or biodegradable materials.

Chapter 2. Reaction of bis (η^6- isomers -dichlorobenzene- η^5-cyclopentadienyliron) with 4,4- Bis (4-hydroxyphenyl) valeric acid hexafluorophosphate.

2.1 Introduction.

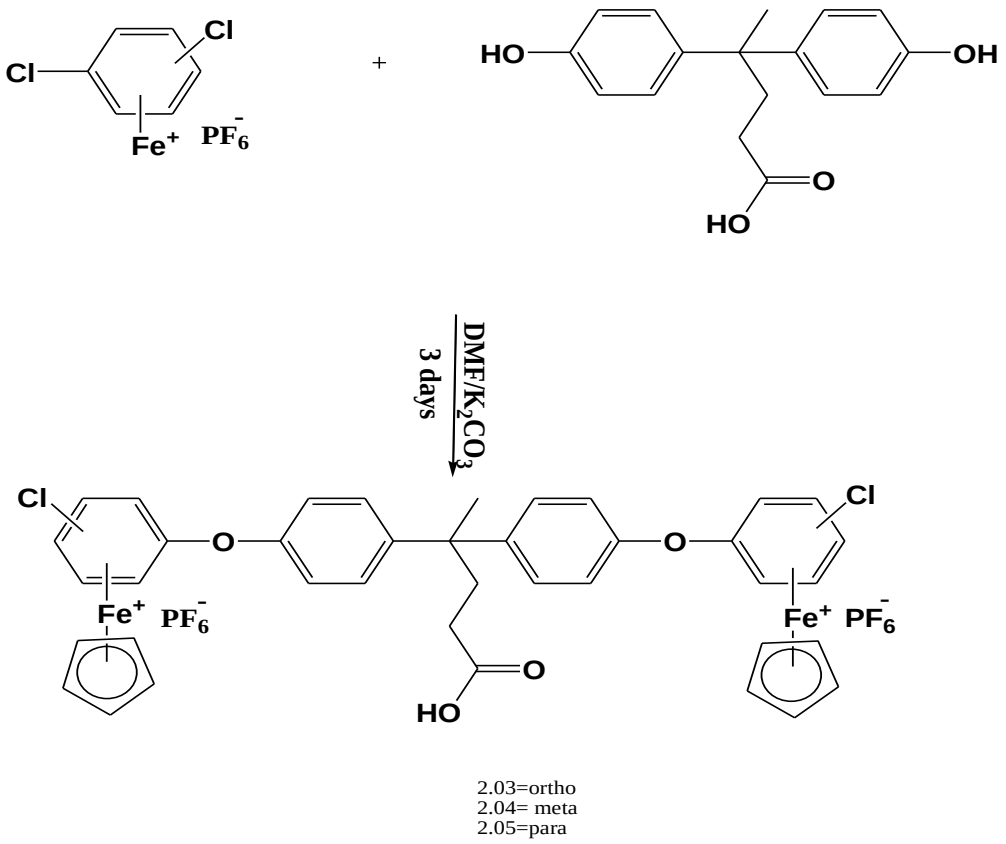
This chapter describes one of the most common routes to the synthesis of bis (cyclopentadienyliron) arene complexes. However, harsh reaction conditions, complicated procedures, low yields and the finite variety of compounds that can be synthesized by one technique show many disadvantages of these methods. Since the development of the chemistry of η^6-arene-η^5-cyclopentadinyliron complexes, enormous attention has been given to the reactivity of halogenated arene complexes. In particular, cyclopentadienyliron activated S_NAr reactions have been confirmed to be a successful method for the production of ether linkages under mild reaction conditions and in good yields. This methodology has been investigated for the synthesis of a variety of symmetric and asymmetric *para-, meta-, and ortho*-cyclopentadienyliron complexes. The flexibility of this technique is further demonstrated by the ability to prepare bis (cyclopentadienyliron) complexes with 4,4-Bis(4-hydroxyphenyl) valeric acid as the desired complex. As will be seen from the subsequent examples, this general process of synthesis allows for the tailored preparation of polymer systems.

2.2 Result and Discussion.

In the course of investigations involving the preparation of bis (cyc1opentadienyiiron) arene complexes with etheric linkages, the synthesis of bimetallic complexes were also achieved. This method has been developed to obtain a good yield. The next example will help to clarify the flexibility and efficiency of this procedure.

2.2.1 Reaction of bis (η^6- isomers-dichlorobenzene-η^5cyclopentadienyliron) with 4,4- Bis (4-hydroxyphenyl) valeric acid hexafluorophosphate.

A reaction of the η^6- isomers -dichlorobenzene-η^5- cyclopentadienyliron (II) hexafluorophosphate complex with a dinucleophile acts as a model to know if a specific dinucleophile will be perfect for bimetallic preparation. Scheme **2.04** represents the capability of the preparation of bimetallic complexes. The dichloro complex, 4,4-bis(4-hydroxyphenyl) valeric acid appears as aromatic carbon present as two symmetric signals in the 120.86-130.53 ppm ranges.



2.03=ortho
2.04= meta
2.05=para

Scheme 2.01: Reaction of bis (η^6- isomers-dichlorobenzene-η^5cyclopentadienyliron) with 4,4- Bis (4-hydroxyphenyl) valeric acid hexafluorophosphate.

1,2-bis(η^6-dichlorobenzene-η^5-cyclopentadienyliron) 4,4- bis (4-hydroxyphenyl) valeric acid hexafluorophosphate (**2.04)**, is synthesized using the same procedure as previously illustrated. In the general, a 2:1 molar ratio of complex to nucleophile was utilized to obtain a desired bimetallic. It was noticed that the yield of this material was approximately 95%.

It is also found that the compound **2.04** and **2.05** were partially soluble in acetone unlike **2.06** . The ^{1}H NMR and ^{13}C NMR and the analytical data for the complex are provided in Table 2.01 and 2.02 .

The spectra of complex **2.04** in comparison with 1,2-bis(η^6-dichlorobenzene-η^5-cyclopentadienyliron)confirms that this reaction was successful. The Cp of complex **2.04** was shifted upfield from 5.40 to 5.22 ppm. The protons of the complex appear in the 6.00-6.99ppm rang, whereas the benzene shows overlapping doublet at approximately 7.70 ppm.

The ^{13}C spectrum is readily analyzed as well. The aliphatic carbon of 4-bis(4-hydroxyphenyl) valeric acids appear in the 27.00-50.00 ppm range. The carbon of the Cp resonates at 80.30 ppm, and the complexed aromatic carbons appear as four distinct signals at 78.09, 84.80, 87.02 and 89.20 ppm. The 4,4-bis(4-hydroxyphenyl) valeric acids aromatic carbon appear as two symmetric signals in the 120.00-130.00 ppm range. Finally, the high field quaternary appearing carbon at 147.32 and 152.00 ppm for the carbon bonded oxygen and carbon attached to the quaternary carbon at 97.80 ppm are a consequence of the C-Cl bond of the aromatic complex ring.

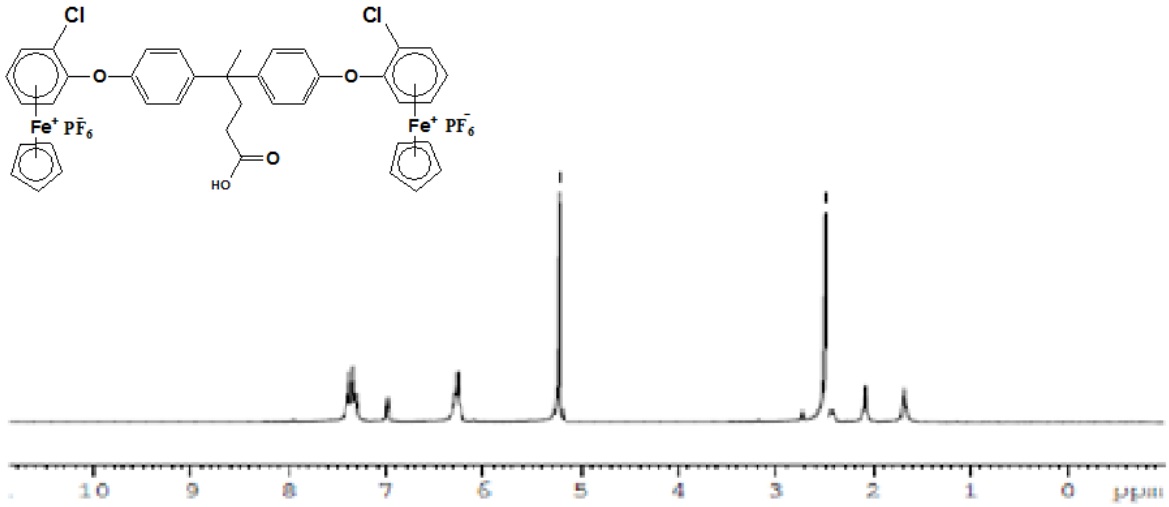


Figure 2.01: ^{1}H NMR of complex **2.04** in DMSO-d_6.

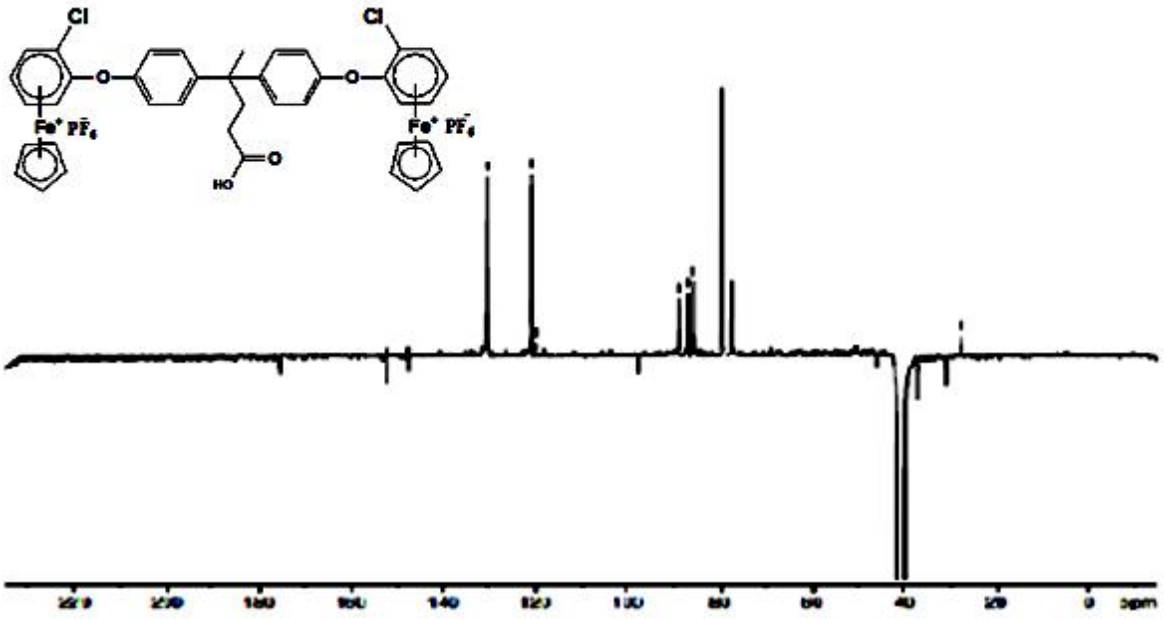


Figure 2.02: ^{13}C NMR of complex **2.04** in DMSO-d_6

Following the same route as the ortho and meta- dichlorobenzene complex, these bimetallic complexes (**2.05)** possess terminal chlorine atoms and hence they can be utilized as building blocks in the synthesis of bimetallic complexes. The yield of these materials is about 95%. In the NMR spectra, the Cp signal has shifted upfield from 5.40 ppm to 5.30ppm. The aromatic complexed protons of the complex **2.05** appears at 6.40 and 6.80 ppm (see Figure 2.05), while the resonance for benzene appears at 7.27ppm.

The ^{13}C NMR as is shown in Figure **2.04** is easily analyzed. The Cp signal is observed at 80.70 ppm. The complexed aromatics appear as two distinct signals at 77.31ppm and 87.70 ppm, while the complexed quaternaries resonate at 104.50 and 133.10 ppm. One also observes two symmetric uncomplexed aromatic signals and their corresponding quaternaries at 121.20, 130.50, 147.60 and 152.10 ppm respectively. The next quaternary that appears at 104.05 ppm is a consequence of the C-Cl bond of the complexed aromatic ring.

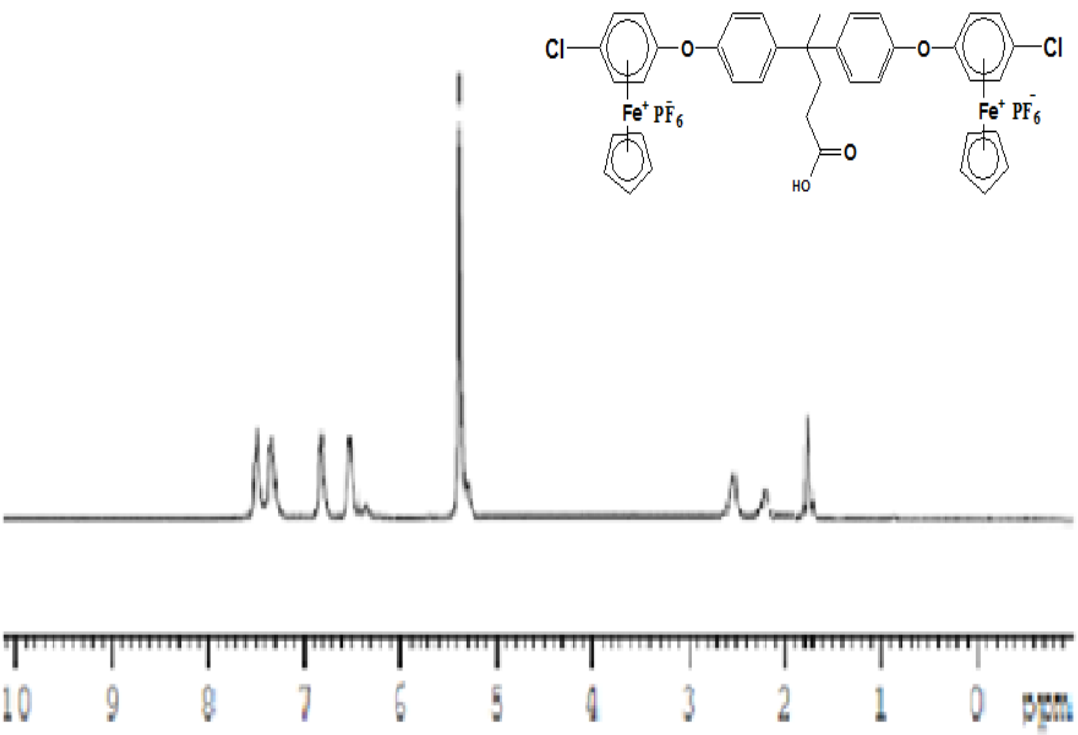


Figure 2.03: ^{1}H NMR of complex **2.04** in DMSO-d_6.

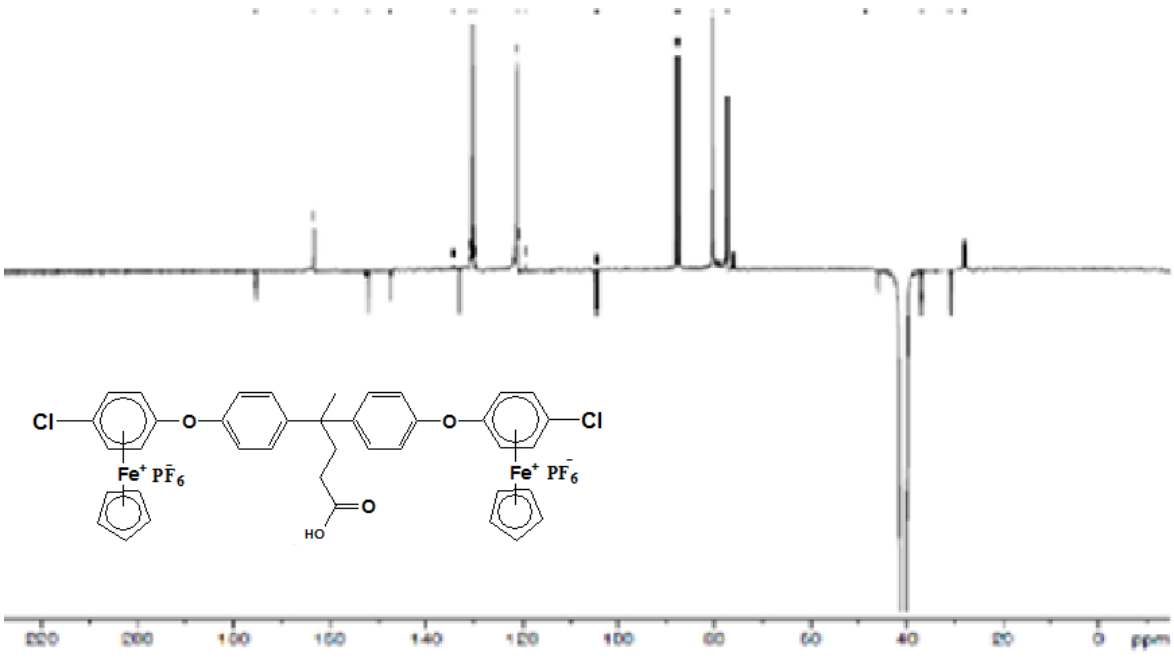


Figure 2.04: ^{13}C NMR of complex **2.04** in DMSO-d_6.

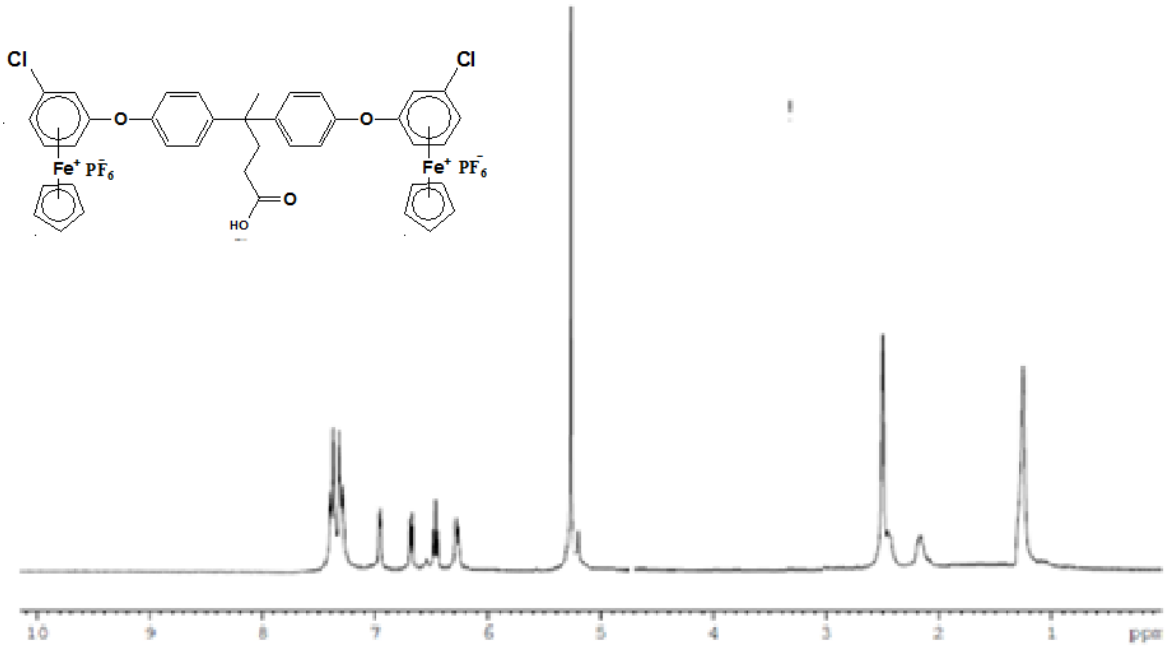


Figure 2.05: ^{1}H NMR of complex **2.05** in DMSO-d_6.

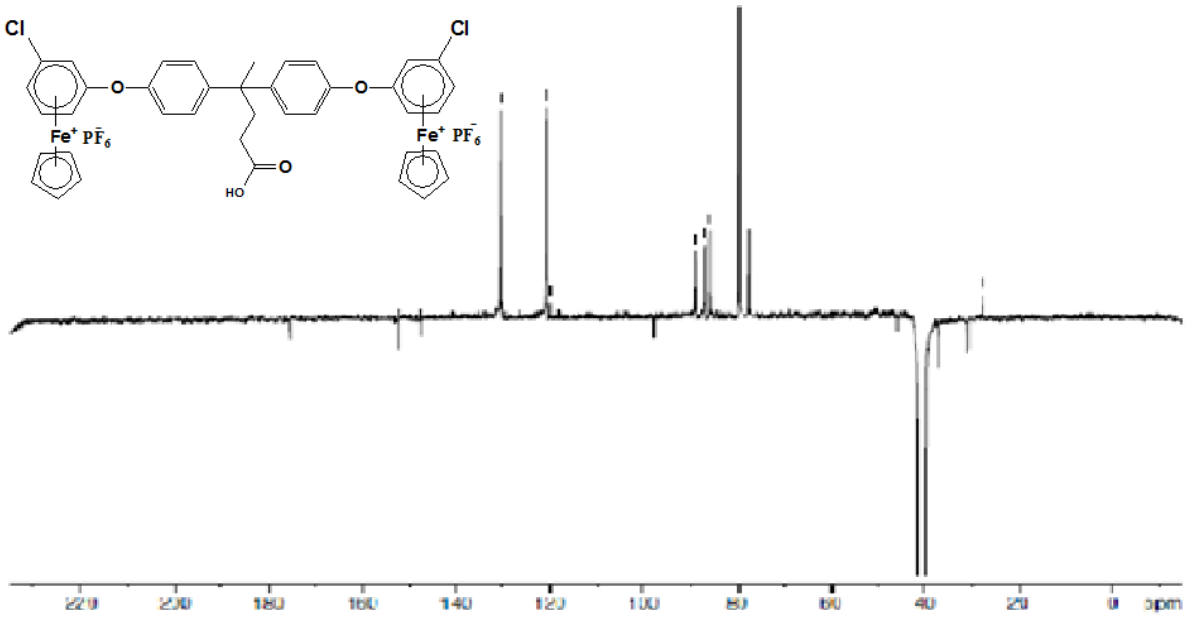


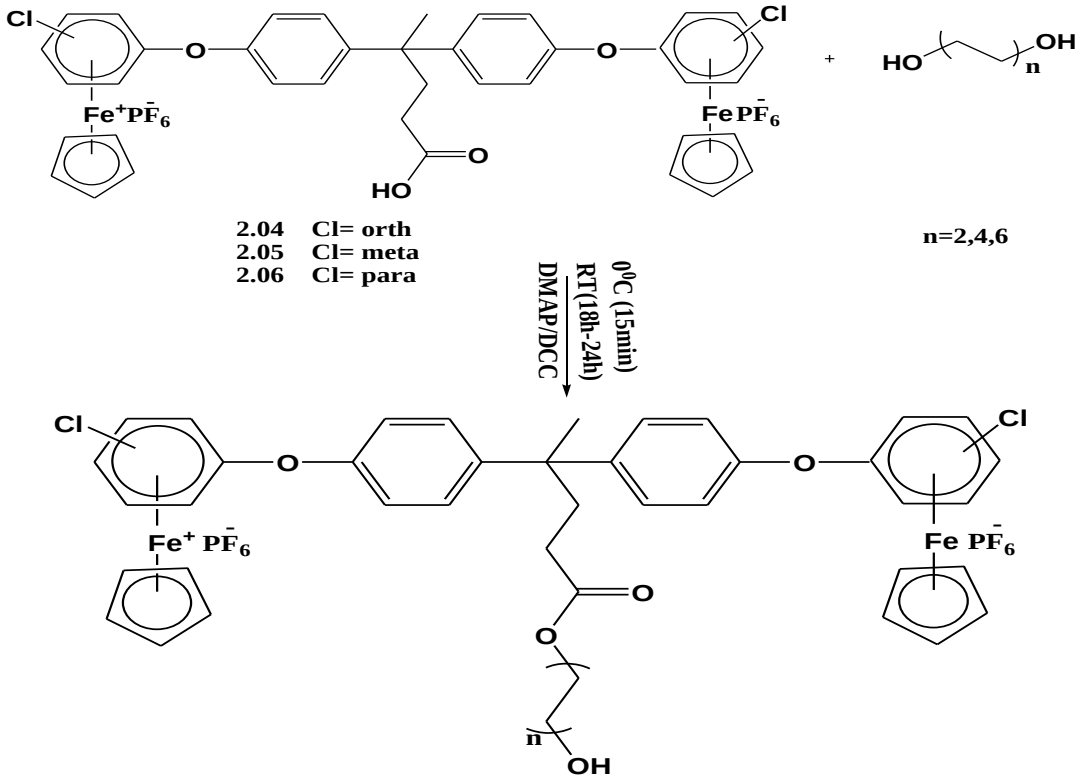
Figure 2.06: ^{13}C NMR of complex **2.05** in DMSO-d_6**.**

Table 2.01: 'H NMR and ^{13}C NMR analysis of complexes 2.4-2.6 in DMSO-d_6

compound	Cp	complexed aromatic	uncompleted aromatic	Others
^{1}H NMR **2.04**	5.23(S,10 H)	6.26(d, *J*= 5.5Hz, 4H) 6.90(d, *J*= 6Hz, 4H)	7.70(dd, , *J*=24 Hz, 8H)	1.67(S,3H) 2.09(S,2H) 2.41(S,2H)
^{13}C NMR **2.04**	80.30	78.09 84.80 87.02 89.20 97.8	120.86 130.53 147.27 152.47	27.80 30.49 36.81 45.70 175.16
^{1}H NMR **2.05**	5.25(S,10 H)	6.20(t.2H) 6.40(S,2H) 6.70(t,2H) 6.96(S,2H)	7.30(dd, *J*=19 Hz 8H)	1.6 (S,3H) 2.09(S,2H) 2.42(S,2H)
^{13}C NMR **2.05**)	79.16	75.85 77.40 85.90 85.20 105.9	119.91 129.16 132.34 151.10 145.84	27.14 29.95 36.21 44.99 175.10
^{1}H NMR **2.06**	5.30(S,10 H)	6.40(t,4H) 6.80(t,4H)	7.27 (dd, , *J*=24, 8H)	1,60(S,3H) 1.98 (S,2H) 2.45(S,2H)
^{13}C NMR **2.06**	80.70	77.30 87.70 104.55 133.10	130.52 121.21 147.63 152.12	27.89 36.00 31.60 37.10 45.70 175.10

2.2.2 Esterification of complexes (2.04-2.06) with length of aliphatic diols

Complexes **2.04-2.06** were reacted with different length of aliphatic alcohols. The synthesis of monomeric units was accomplished using the methodology employed in Scheme 1.18. A condensation reaction of the carboxylic acid functionalized diiron complexes with various lengths of diols allowed for the synthesis of complexes with terminal alcohol. It was found that increasing the length of aliphatic chains resulted in more soluble materials.



Scheme 2.02 Synthesis of complexes **2.07- 2.15**

Identification of the complex and monomer molecules was achieved utilizing NMR spectroscopic analysis. Table 2.02 shows ^{1}H NMR spectra of complexes **2.10-2.15**.

It can be seen that the two spectra revealed some similarities. The spectra provided evidence that the condensation reaction had preceded successfully. For instance, the appearance of the OH for complex **2.08** resonating at 3.33 ppm in the monomer spectrum confirms that this reaction was successfully performed. The aromatic protons of the uncomplexes appear at approximately 7.33 ppm while the complexed aromatic protons resonate between 6.20 and 7.04 ppm. The intense singlet around 5.23 ppm in each spectrum represents the five-cyclopentadienyl protons of the metal moiety. The four ether protons appeared next to ester and alcohol appear at 4.40 and 3.98 ppm respectively, one in the range of 2.14-2.22 ppm, and the other aliphatic protons appear in the 1.22 ppm- 2.57 ppm ranges.

The ^{13}C NMR as is shown in Figure **2.08** is strightforward to analyze. The Cp signal is appeared at 79.94 ppm. The complexed aromatics observe as two distinct signals at 77.88, 85.69, 86.74, 88,77 ppm,. One also observes two symmetric uncomplexed aromatic signals and their corresponding quaternaries at 120.67, 130.23 , 147.25 and 152.23 ppm respectively. The next quaternary

that observes at 96.50 ppm is a consequence of the C-Cl bond of the complexed aromatic ring.

Table 2.02: ^{1}H NMR ^{13}C NMR analysis of complexes **2.07- 2.15** in DMSO d_6.

compound	Cp(ppm)	complexed aromatic(ppm)	uncomplexd aromatic(ppm)	Others(ppm)
2.07 ^{1}H	5.27(S,5H)	6.30(S,4H) 6.80(S,4H)	7.20(D,8H, *J*= 5.8Hz)	1.60(S,3H) 2.00(S,2H) 2.50(S,2H) 3.30(S,1H) 4.00(S,2H) 4.40(S,2H)
2.07 ^{13}C	79,04	76.98 84.80 85.74 87.88 96.13	119.15 129.28 161.46 151.13	24.60 25.80 27.50 31.41 38.93 43.52 64.20 62.32 174.00
2.08 ^{1}H	5.23	6.27(S,2H) 7.04(S,2H)	7.33(D,8H, *J*= 5.3Hz)	2.45(S,2H) 2.05(S,2H) 1.00- 1.80(M,15H) 3.30(S,H) 3.98(S,2H) 4.40(S,2H
2.08 ^{13}C	79.94	77.88 85.69 86.74 88.77 96.50	130.23 120.67 147.25 152.23	27.89 29.95 31.75 33.58 34.22 45.76 64.89 61.51
2.09 ^{1}H	5.27	6.27(S.2H) 7.04(S,2H)	7.33(D,8H, *J*= 6.1Hz)	2.45(S,2H) 2.05(S,2H) 1.00- 1.80(M,21H) 3.30(S,1H) 4.00(S,2H) 4.40(S,2H)
2.09 ^{13}C	79.94	77.88	130.00	25.30

		85.69 86.74 88.77 96.70	120.67 147.25 152.23	26.20 27.89 29.95 34.22 36.80 31.75 45.76 174.81 33.58 64.89 61.51
2.10 ^{1}H	5.29	6.30(S.2H) 6.50(S,2H) 6.83(S,2H) 7.00(S,2H)	7.30(D,8H ,*J*= 6.12Hz)	1.00-1.80(M,7H) 2.00(S,2H) 2.50(S,2H) 3.3(S,1H) 4(S,2H) 4.4(S,2H
2.10 ^{13}C	79.05	77.21 76.21 86.90 86.31 106.45	120.90 130.19 157.16 152.01	25.40 28.01 31.5 38.12 64.898 61.51 172.33
2.11 ^{1}H	5.27(S,5H)	6.1(S.2H) 6.30 (S,2H) 6.70(S,2H) 7.00(S,2H)	7.30(D,8H *J*= 5.32Hz)	1-1.8(M,15H) 1.98(S,2H) 2.50(S,2H) 3.3(S,1H) 4(S,2H) 4.4(S,2H
2.11 ^{13}C	79.05	73.11 73.11 86.7 86.26 106.35	120.9 130.19 157.16 152.01	25.90 30.50 31.50 38.12 41.15 64.89 61.51

				174.33
2.12 ^{1}H	5.27(S,5H)	6.11(S.2H) 6.32(S,2H) 6.70(S,2H) 7.00(S,2H)	7.30(D,8H)	1-1.8(M,21H) 2.00(S,2H) 2.50(S,2H) 3.30(S,1H) 4.00(S,2H) 4.40(S,2H
2.12 ^{13}C	79.05	77.51 76.92 86.26 86.70 106.49 132.23	120.90 130.19 157.16 152.01	25.72 25.12 30.50 32.30 34.51 38.12 64.89 61.20 172.06
2.13 ^{1}H	5.23(S,5H)	6.40(S,4H) 6.70(S,4H)	7.33(S,8H)	1.44(S,4H) 1.60(S,3H) 1.98 (S,2H) 2.45(S,2H) 3.41(S,1H) 4.10(S,2H) 4.45(S,2H)
2.13 ^{13}C	79.26	86.77 76.31 103.55 131.92	129.28 120.12 146.22 150.99	26.97 36.00 29.78 45.09 24.86 28.84 60.24 63.97
2.14 ^{1}H	5.28	6.41(S,4H) 6.79(S,4H)	7.26(D,8H)	1-1.8 (M,15H) 2 (S,2H) 2.45(S,2H) 3.41(S,1H) 4.10(S,2H) 4.45(S,2H)

2.14 ^{13}C	80.21	77.26 87.66 104.50 131.23	121.01 132.89 152.15 147.22	26.28 45.92 36.91 29.53 29.68 28.92 25.13 26.21 61.57 64.90
2.15 ^{1}H	5.24	6.41(S,4H) 6.79(S,4H)	7.26(D,8H)	1-1.8 (M,121H) 1.95(S,2H) 2.45(S,2H) 3.41(S,1H) 4.10(2H) 4.45(S,2H
2.15 ^{13}C	80.06	77.26 87.66 104.5 131.23	121.01 132.89 152.153 147.22	26.28 45.925 36.91 29.53 29.68 28.92 25.13 26.213 61.57 64.92

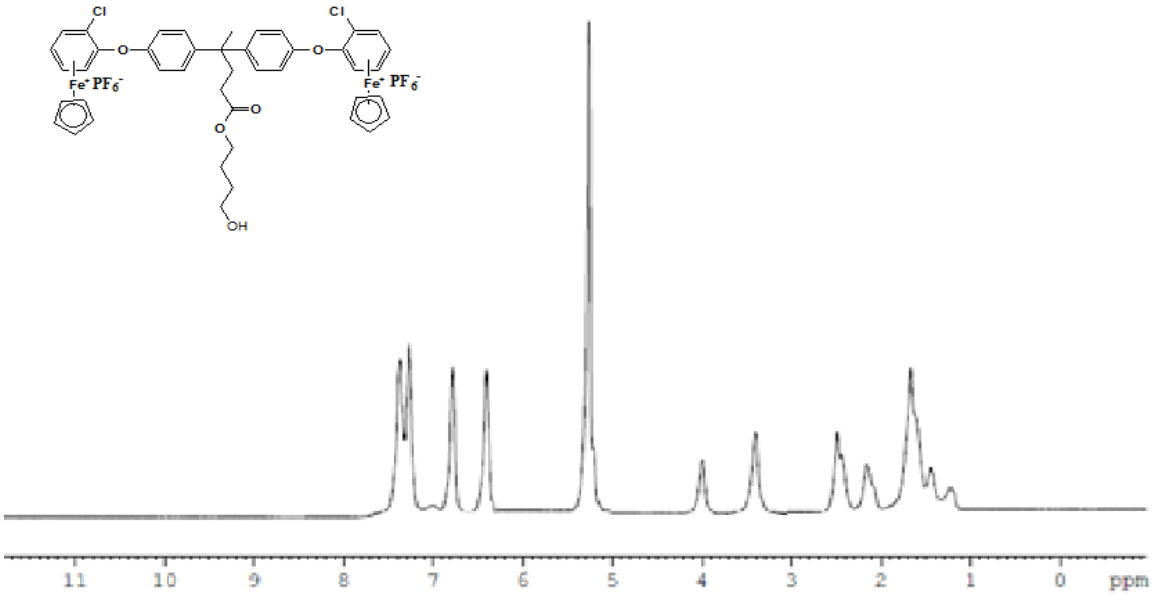


Figure 2.07 : ^{1}H NMR of complex **2.07** in DMSO $d_{6.}$

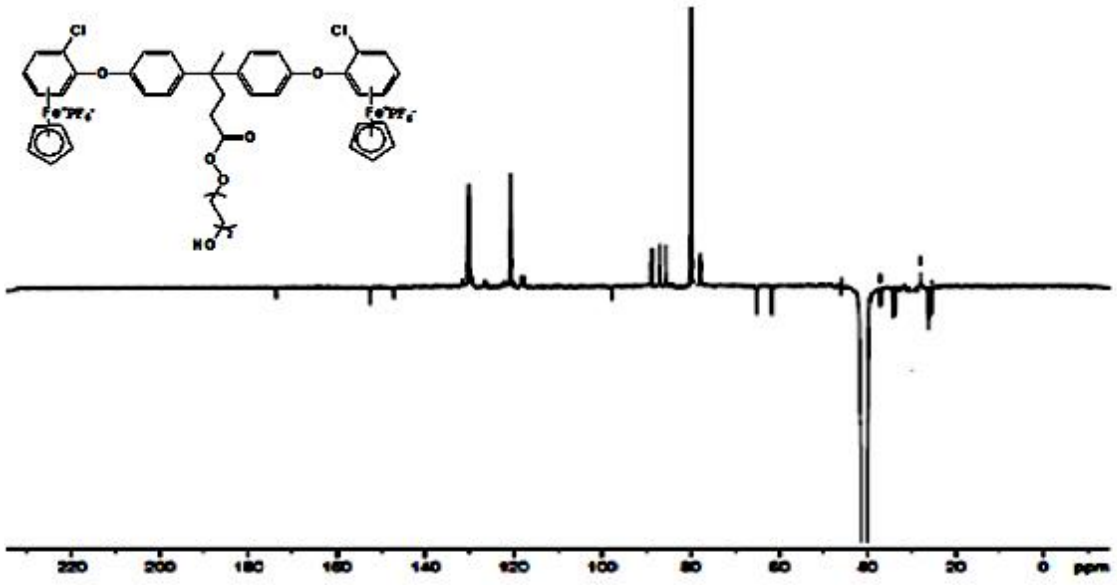


Figure 2.08: ^{13}C NMR of complex **2.07** in DMSO d_6.

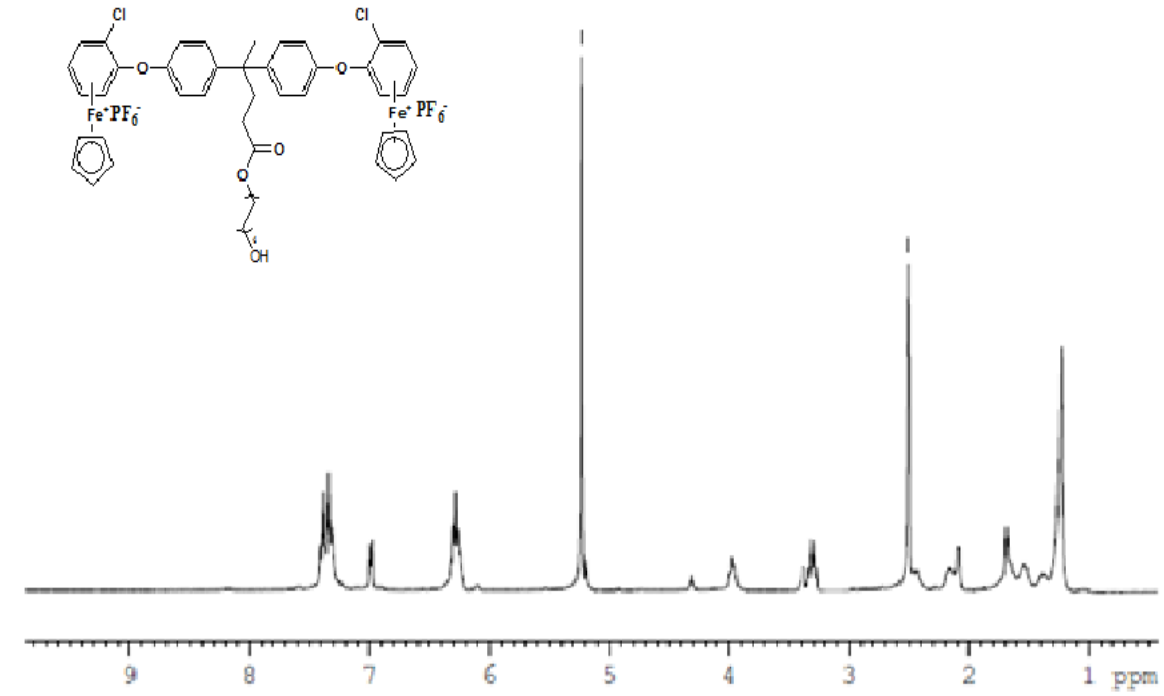


Figure 2.09: ^{1}H NMR of complex **2.08** in DMSO $d_{6.}$

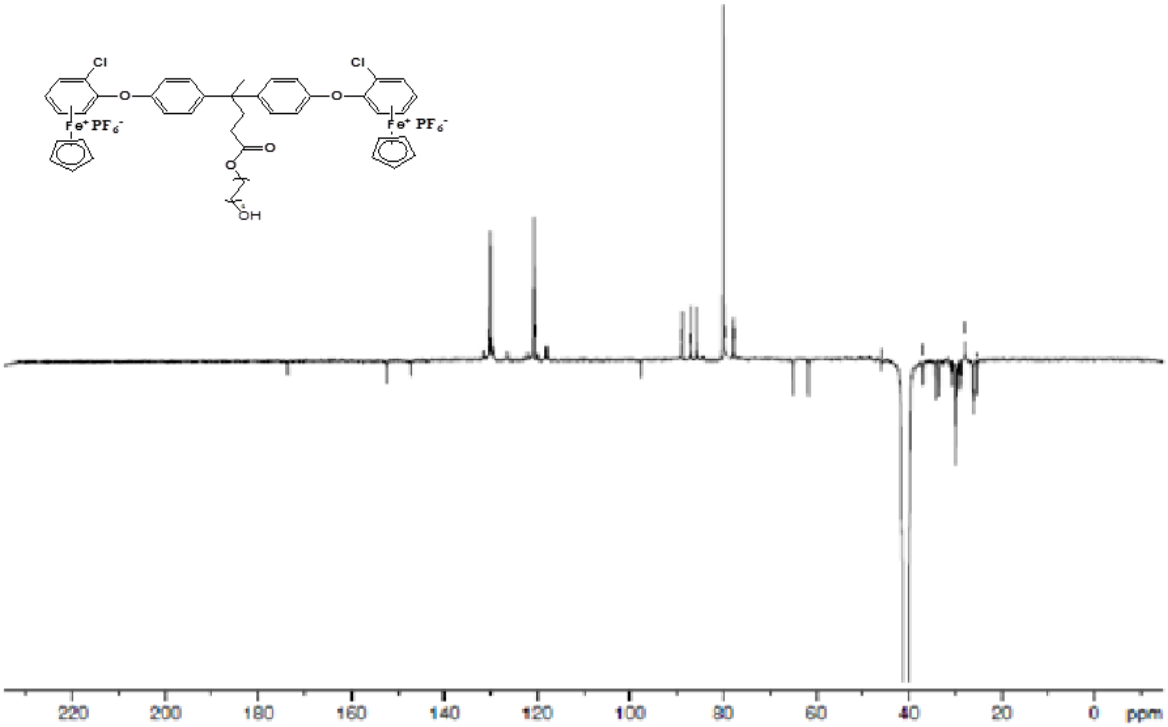


Figure 2.10: ^{13}C NMR of complex **2.08** in DMSO $d_{6.}$

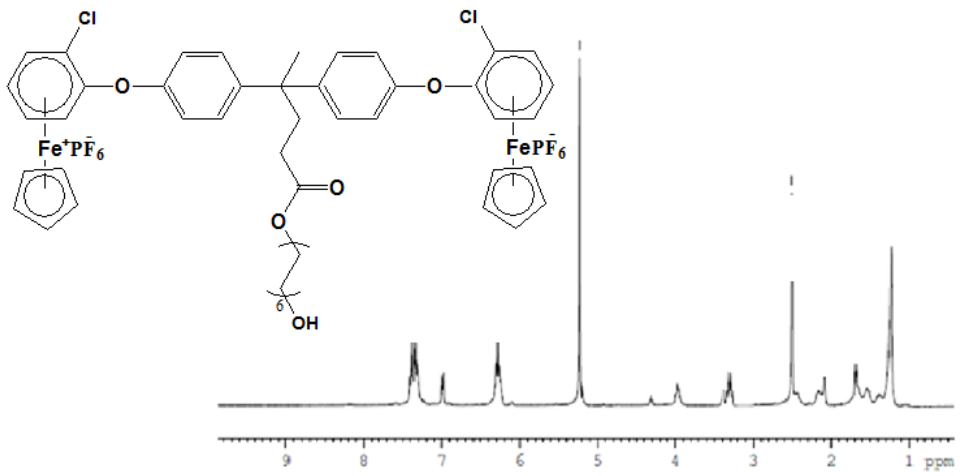


Figure 2.11: ^{1}H NMR of complex **2.09** in DMSO $d_{6.}$

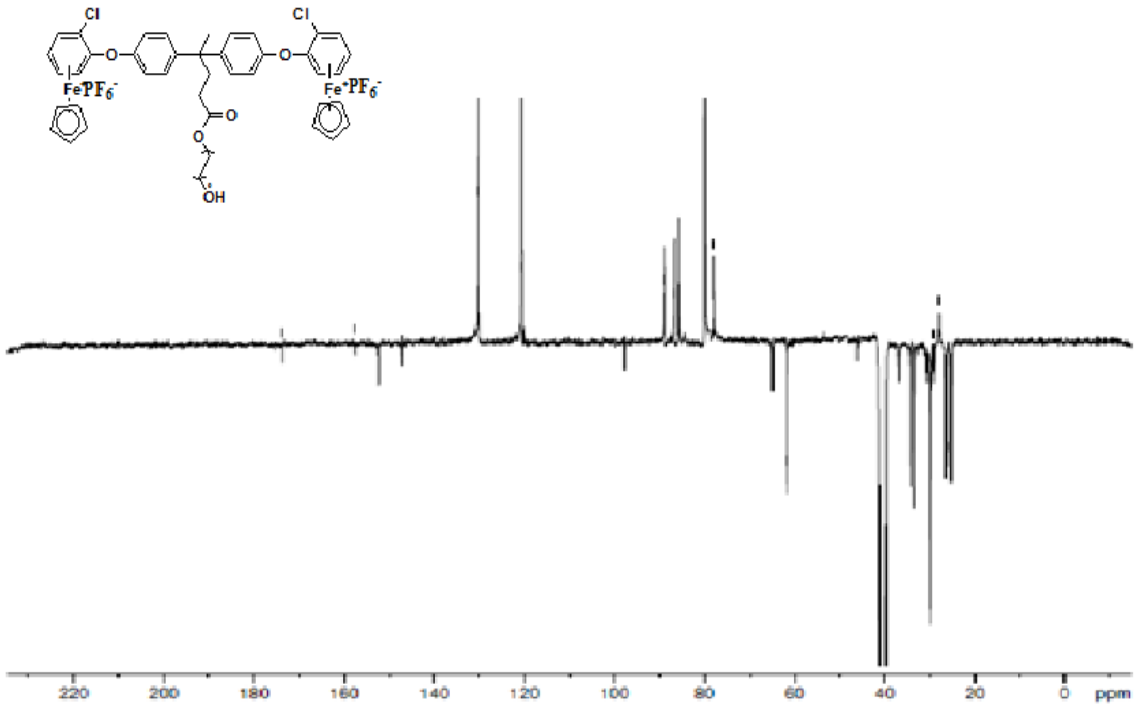


Figure 2.12: ^{13}C NMR of complex **2.09** in DMSO $d_{6.}$

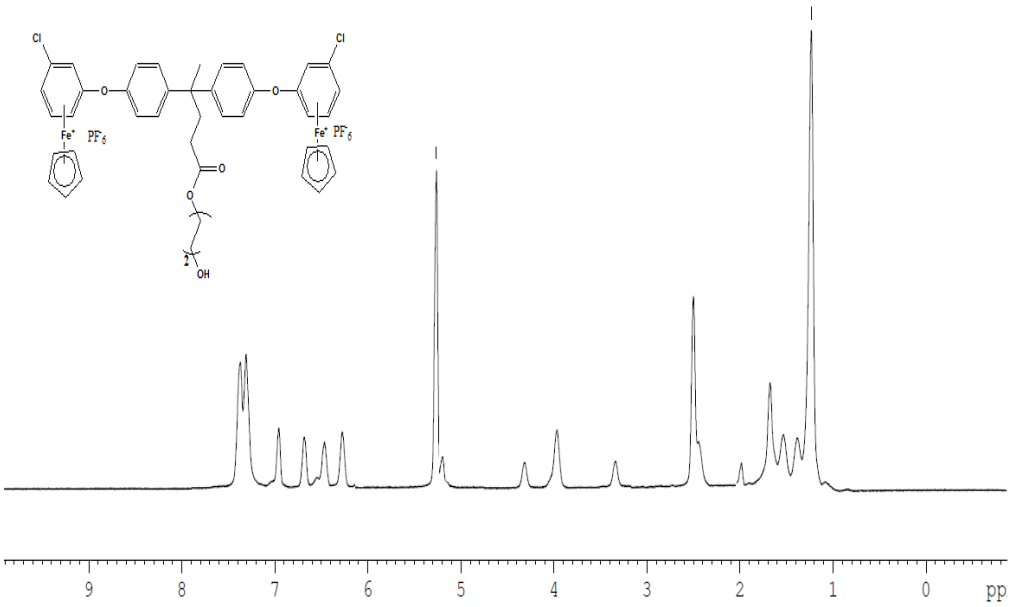


Figure 2.13: ^{11}H NMR of complex **2.10** in DMSO $d_{6.}$

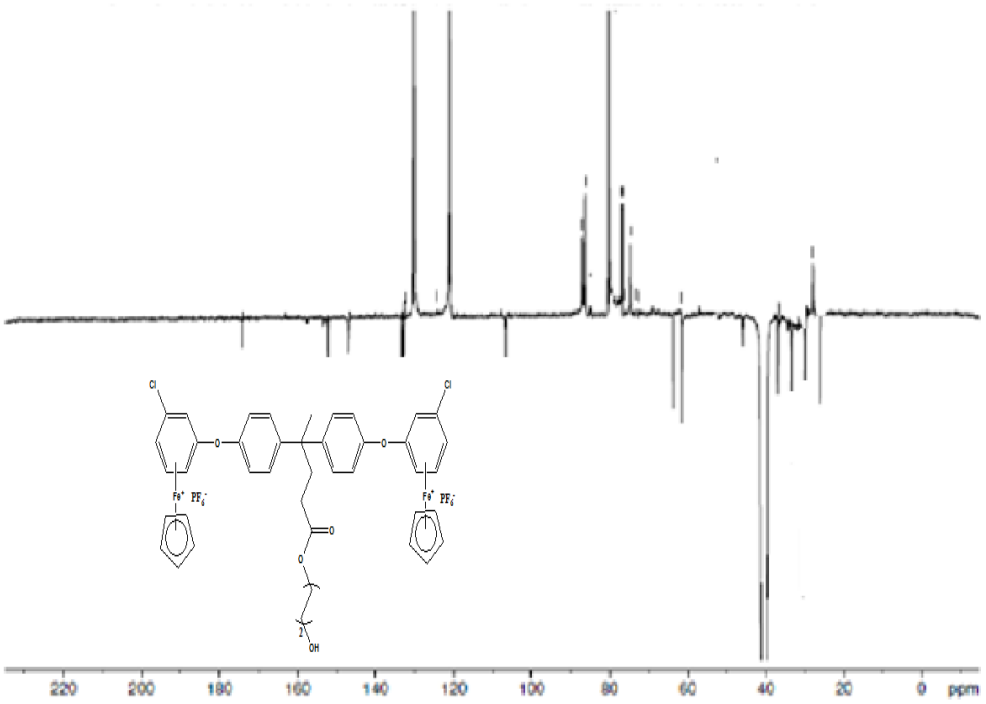


Figure 2.14: ^{13}C NMR of complex **2.10** in DMSO $d_{6.}$

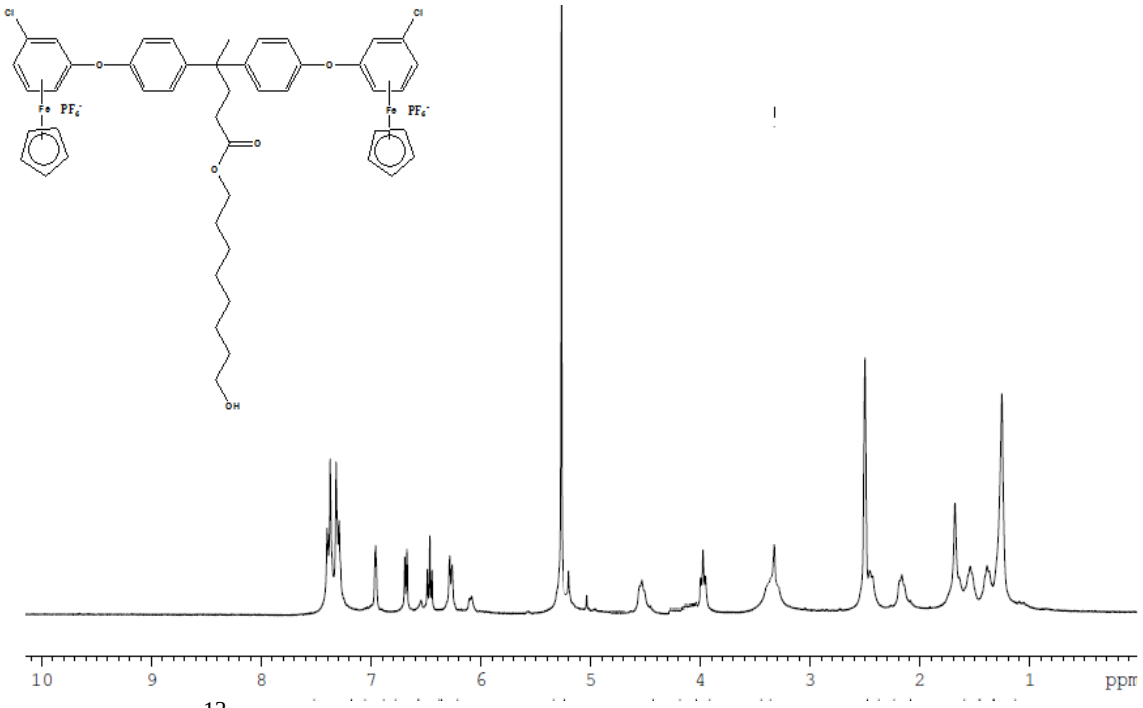


Figure 2.15: ^{13}H NMR of complex **2.11** in DMSO d_6.

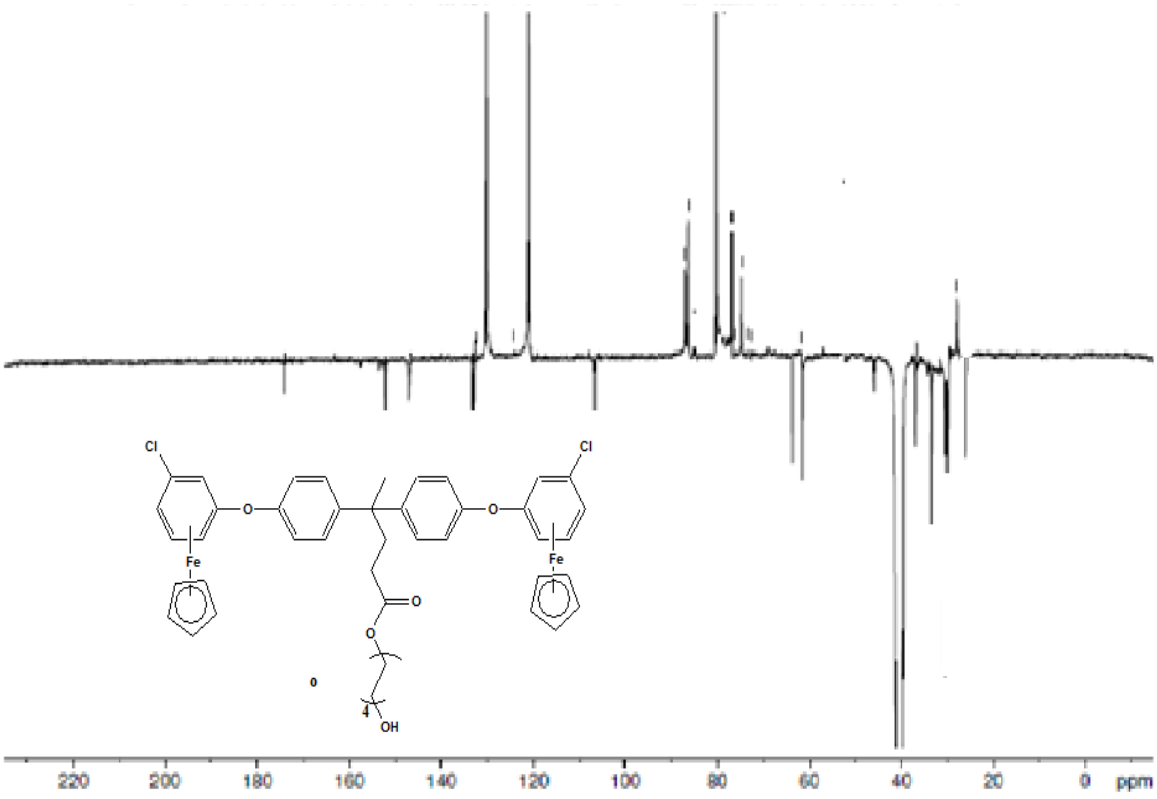


Figure 2.16: ^{13}C NMR of complex **2.11** in DMSO d_6.

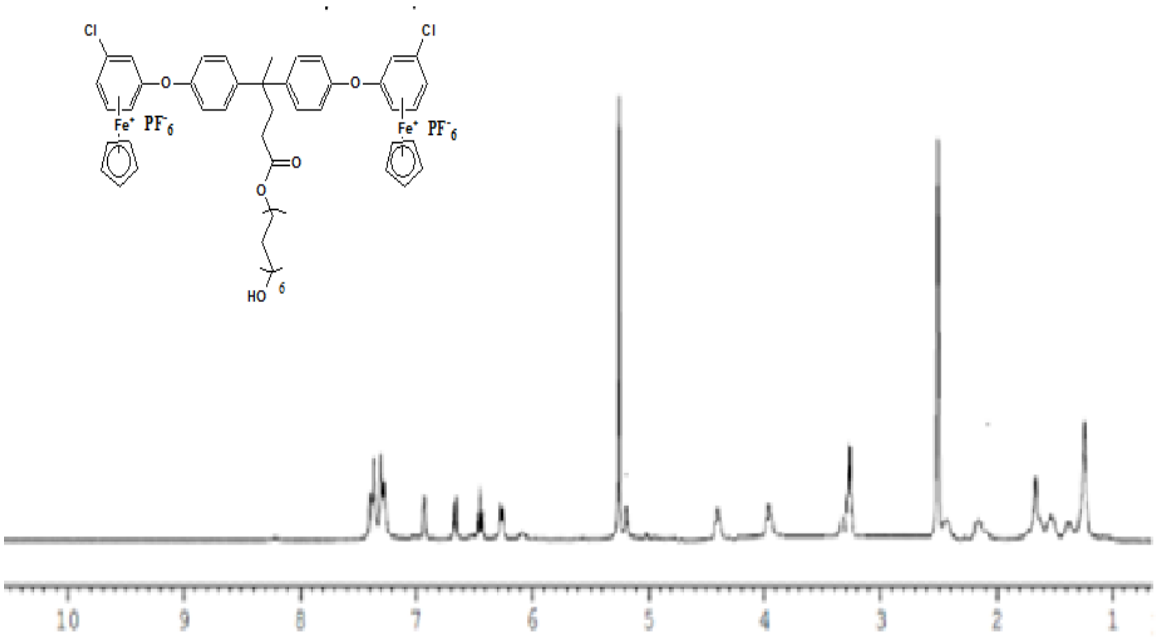


Figure 2.17: ^{1}H NMR of complex **2.12** in DMSO $d_{6.}$

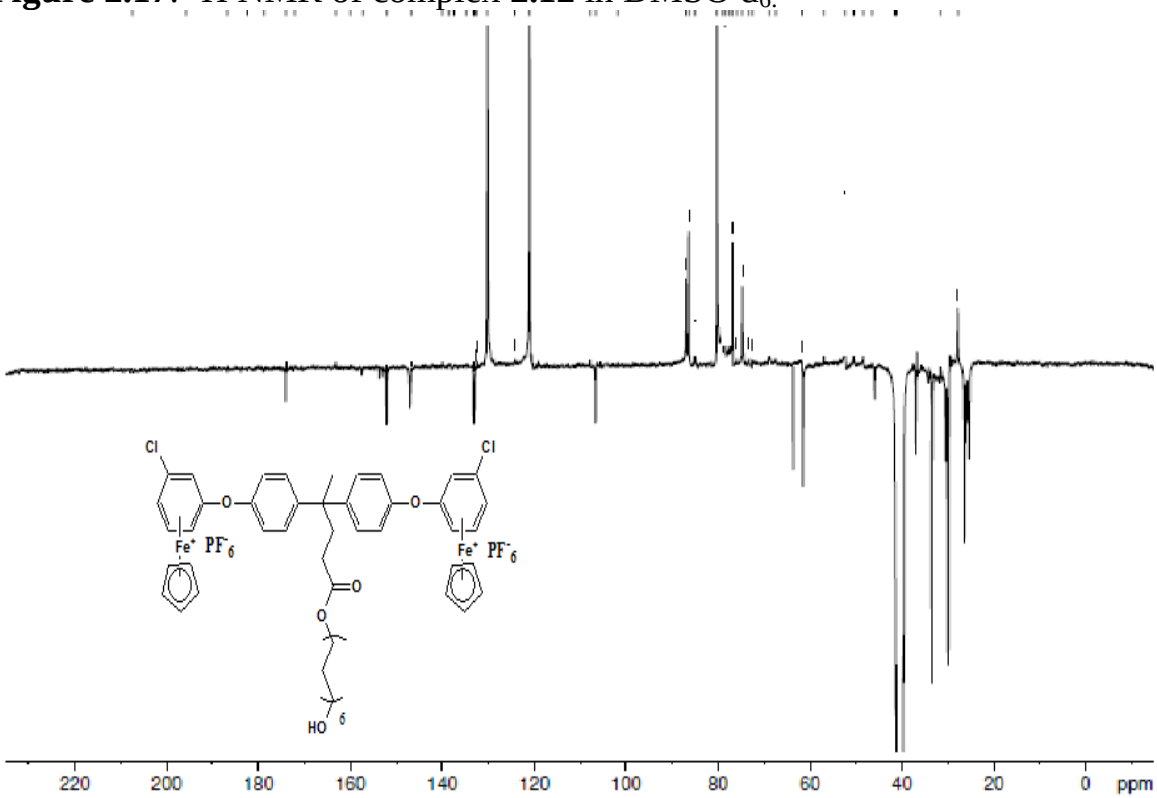


Figure 2.18: ^{13}C NMR of complex **2.12** in DMSO $d_{6.}$

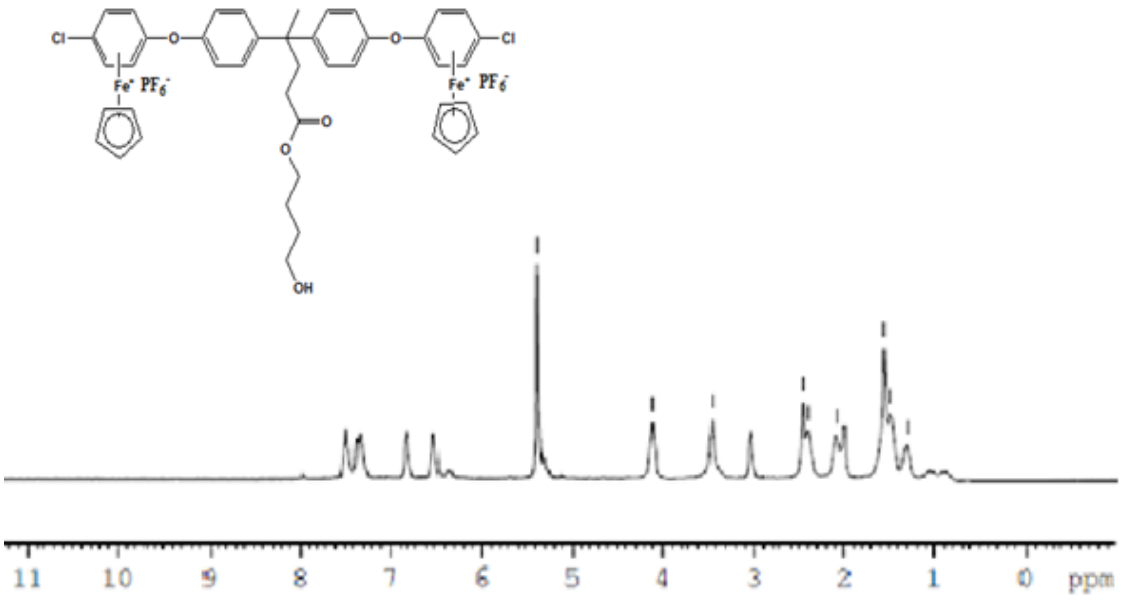


Figure 2.19: ^{1}H NMR of complex **2.13** in DMSO $d_{6.}$

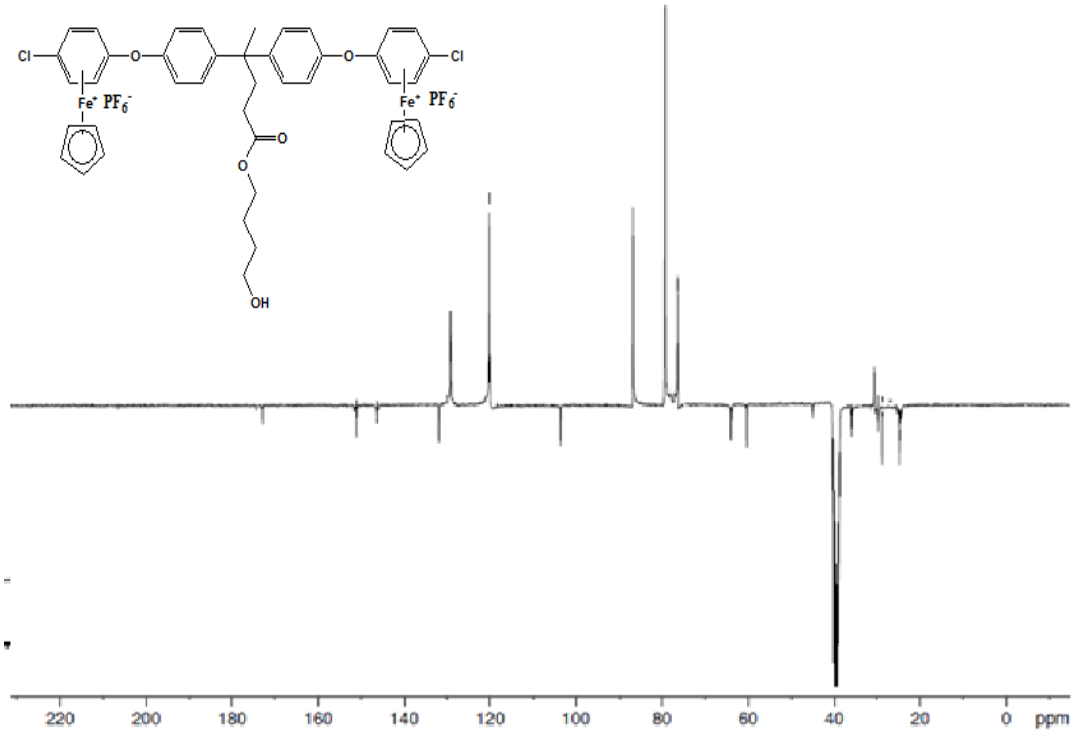


Figure 2.20: ^{13}C NMR of complex **2.13** in DMSO $d_{6.}$

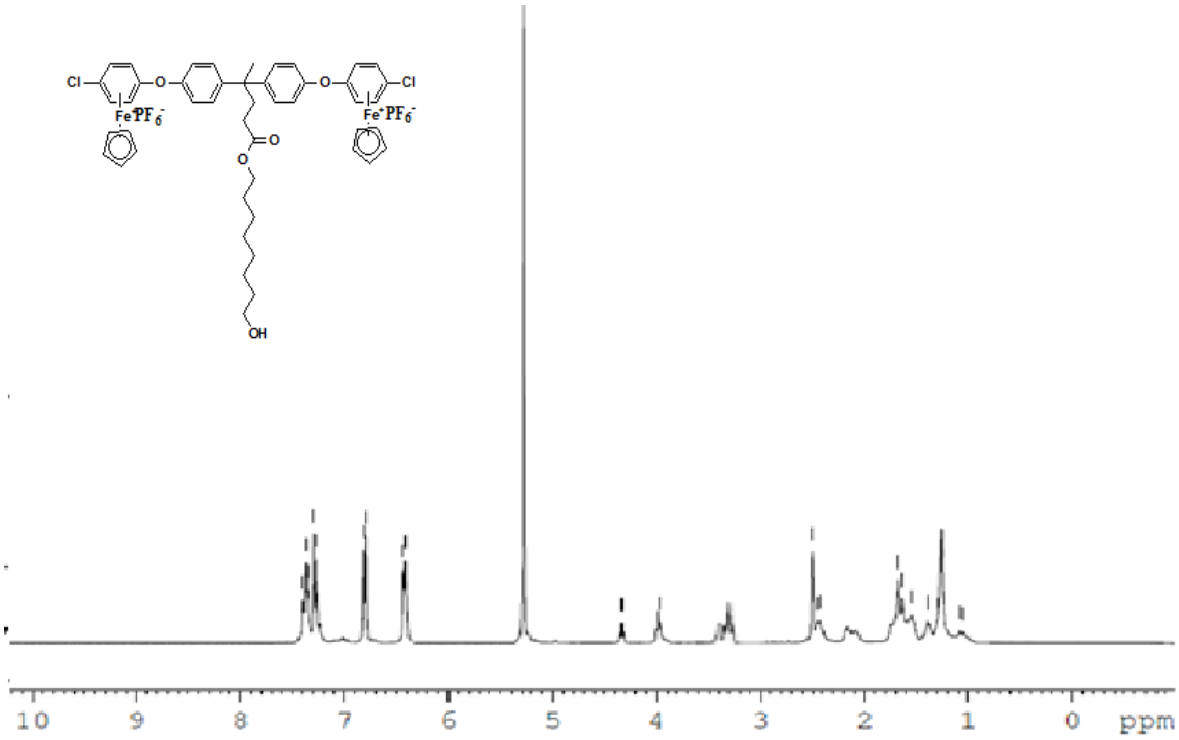


Figure 2.21: ^{1}H NMR of complex **2.14** in DMSO $d_{6.}$

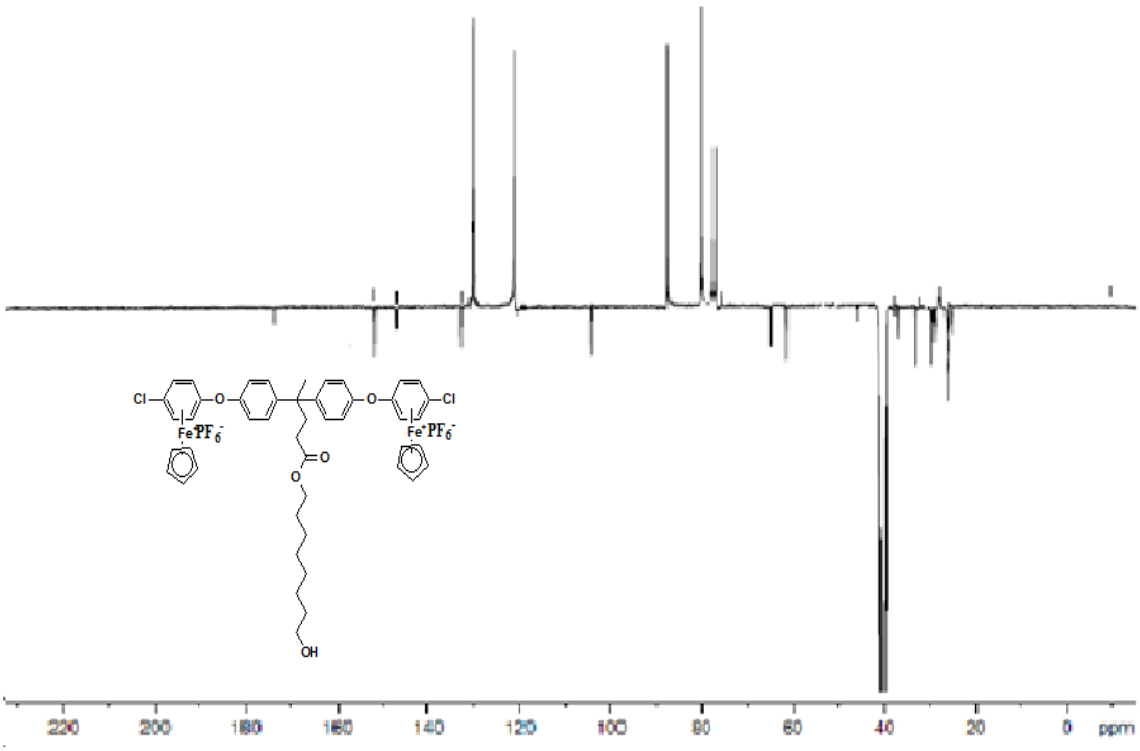


Figure 2.22: ^{13}C NMR of complex **2.14** in DMSO $d_{6.}$

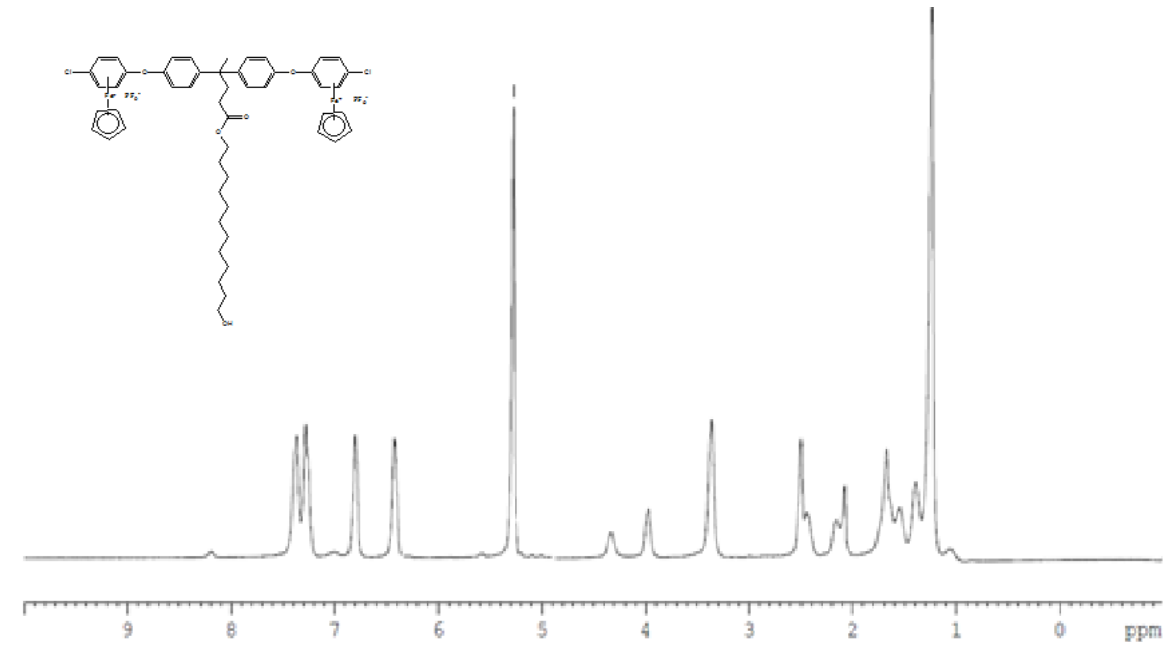


Figure 2.23: ^{1}H NMR of complex **2.15** in DMSO $d_{6.}$

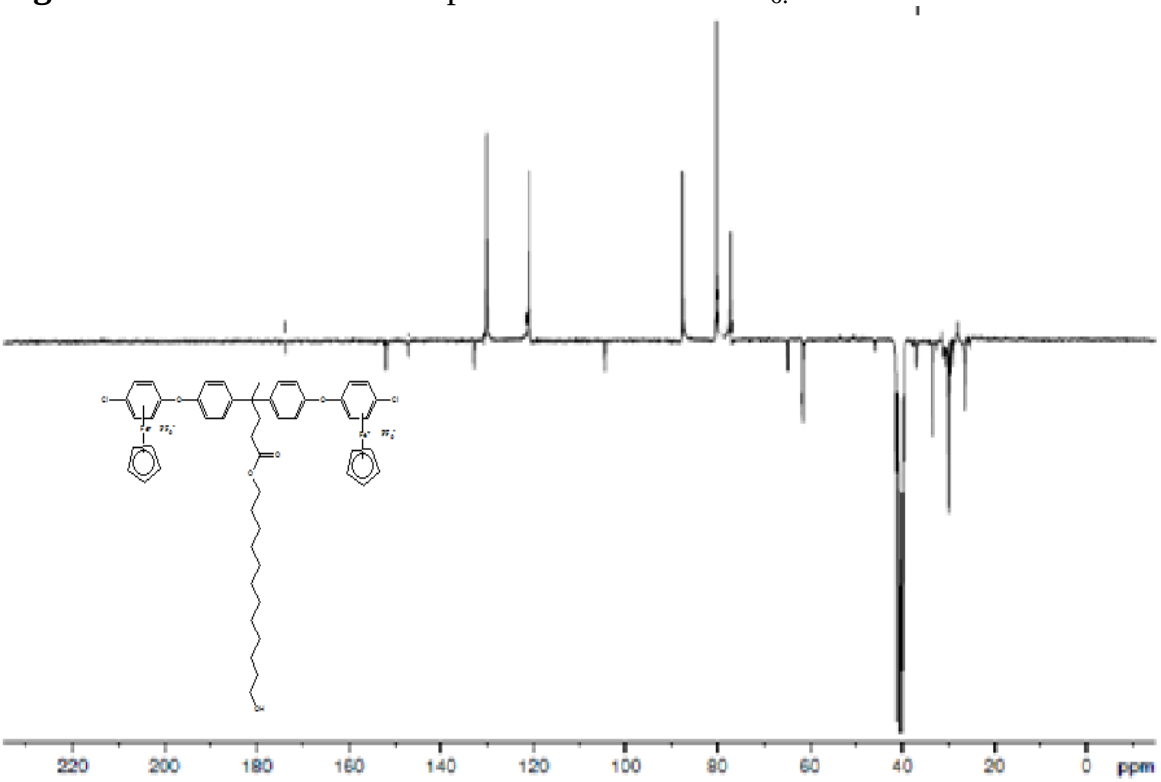


Figure 2.24: ^{13}CNMR of complex **2.15** in DMSO $d_{6.}$

2.2.2.1 Thermal Properties of the complexes.

The thermal properties of the metallated compound **2.09** were investigated applying thermogravimetric analysis (TGA) as illustrated in Figure **2.16**. The thermograms provide information from about the thermal stability of these materials by measuring their weight losses when they are heated. All of the metalled compounds shows a 17.24 to 33.54%weight loss between 219 and 260 °C, corresponding the cleavage of the cyclopentadienyliron hexafluorophosphate. Following this first weight loss step, the compound underwent a second weight loss that was dependent upon the aromatic linkages in their backbones. Compound **2.09** also displayed a 44.41 % weight loss beginning at 290°C, which is consistent with its rigid aromatic backbone.

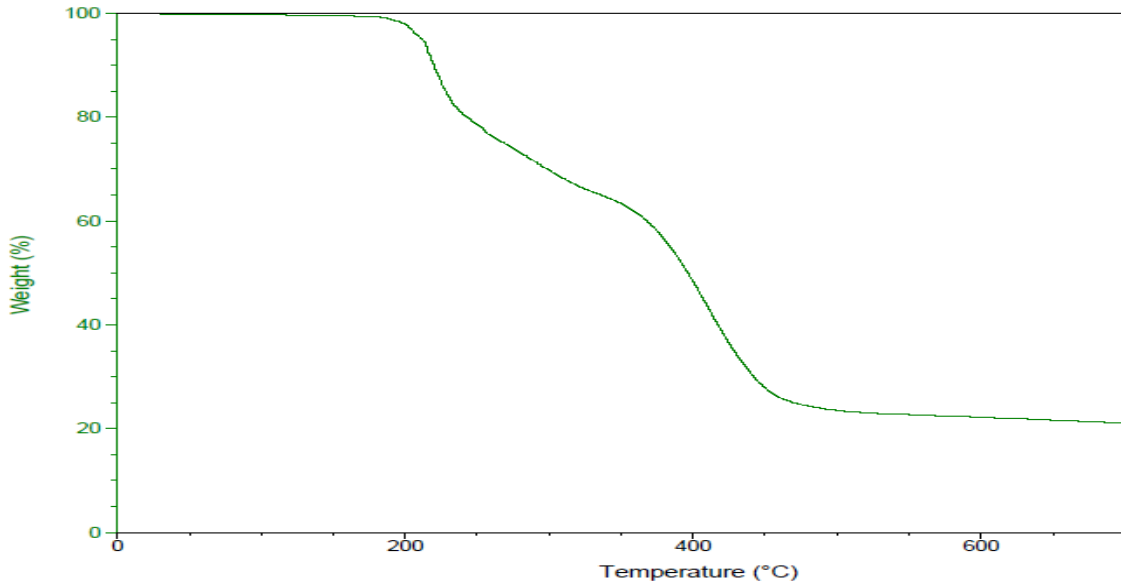


Figure 2.25: Thermogram of the compound **2.09** in nitrogen

2.2.2.2 Scanning Electron Microscopy.

The surface texture as displayed in a film was investigated for the series of complexes by scanning electron microscopy. Representative surface morphology of the samples is shown in Figure **2.17**. At high magnification, the micrograph of complex **2.07** had a fine globular appearance. The micrographs of complex **2.08** and **2.02** appeared as distinct layer with smooth edges and some porous morphology was observed.

Complex .

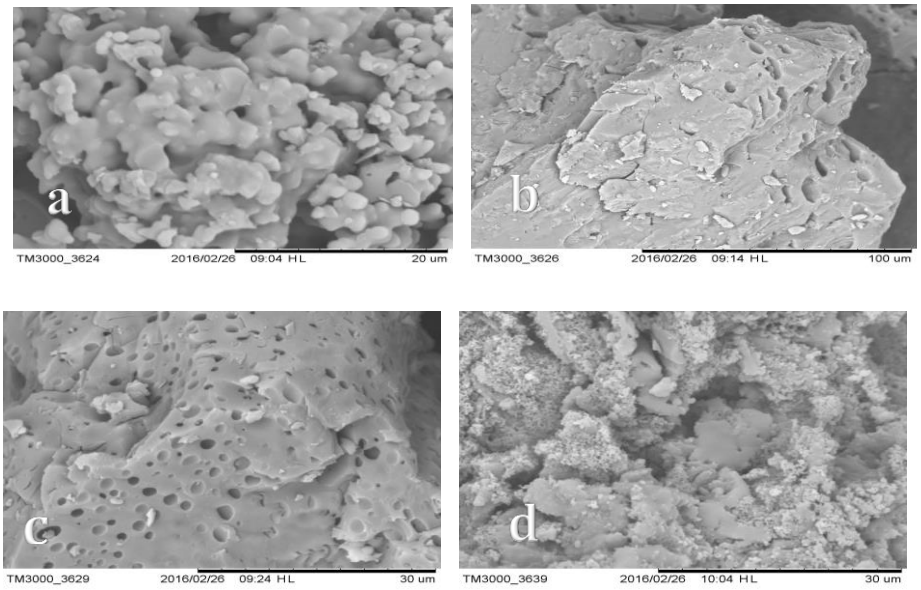
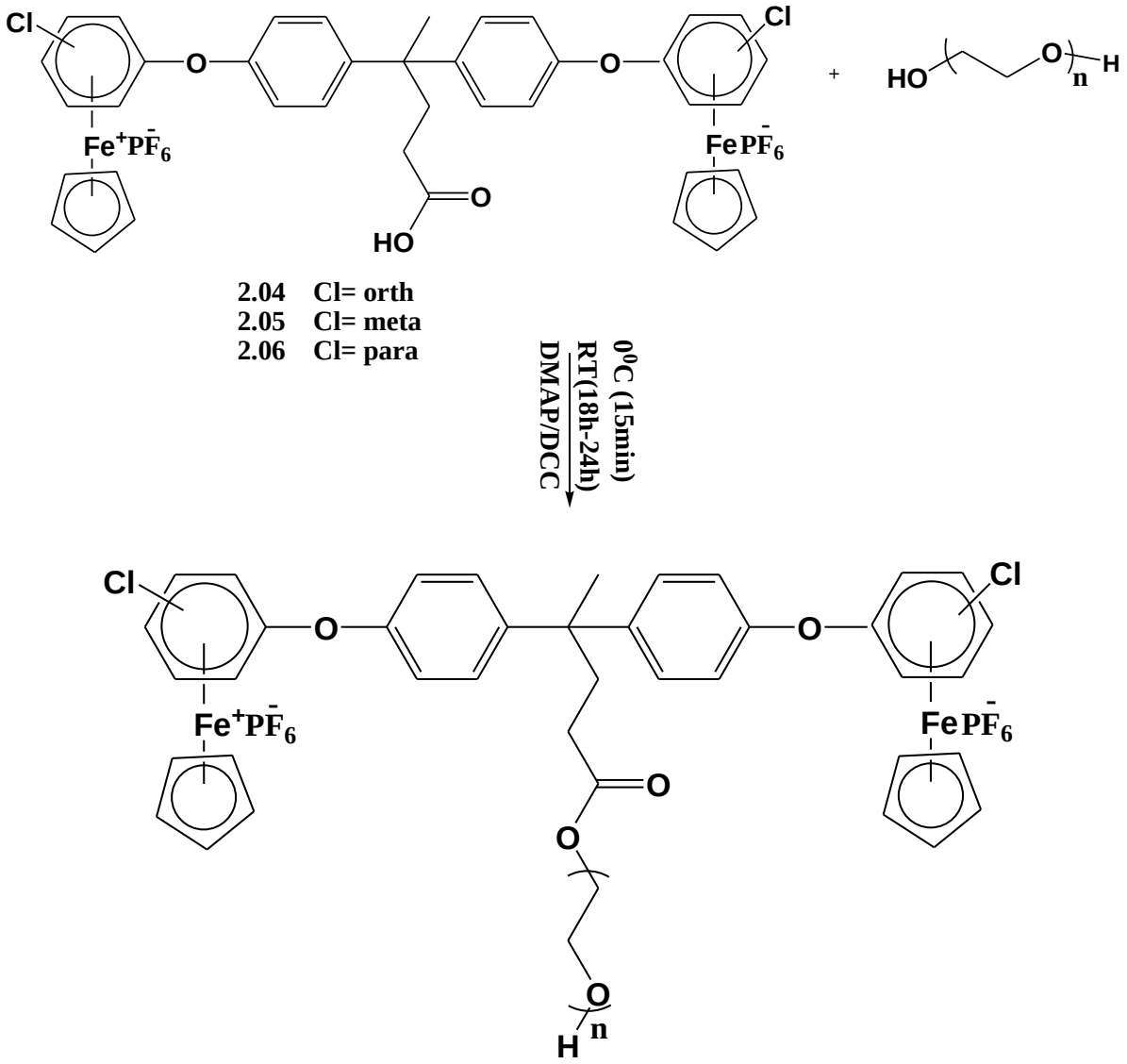


Figure 2.26: Scanning electron micrographs of a)2.07 b) 2.08 c) 2.09 and 2.02 complexes

2.2.3 Reaction of bimetallic Isomers of with polyethylene glycol (PEG) (Preparing the prerequisite micelles).

Polyethylene glycol (PEG) is a polyether compound with multiple various applications from industrial manufacturing to medicine. PEG is also known as polyethylene oxide (PEO) or polyoxyethylene (POE), depending on its molecular weight. The structure of PEG is commonly expressed as $H{-}(O{-}CH_2{-}CH_2)_n{-}OH$. Isomers of bis($\eta^6$-dichlorobenzene-$\eta^5$-cyclopentadienyliron) 4,4- bis(4-hydroxyphenyl) valeric acid hexafluorophosphate was reacted with polyethylene glycol with a molecular weight of approximately 2000 in order to produce **prerequisite micelles**. The synthesis of monomeric units was accomplished using the methodology employed in Scheme **2.03,** a condensation reaction of the carboxylic acid functionalized diiron complexes with PEG allowing for the synthesis of complexes with terminal alcohols terminal. It was found that these compounds (**2.16-2.18)** dissolve even in water.



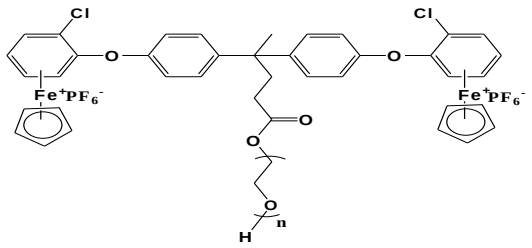
2.04 Cl= orth
2.05 Cl= meta
2.06 Cl= para

2.16 Cl= orth
2.17 Cl= meta
2.18 Cl=para

Scheme 2.03: Synthesis of complexes **2.16- 2.17.**

These materials were obtained in yields of approximately 95%. In the spectra ^{1}H NMR of compound **2.16** spectra, the Cp moved upfield from 5.28 ppm to 5.23 ppm. The complexed protons of the compound **2.16** appear at

6.28- 6.90 ppm, while resonance for uncomplexed aromatic appears at 7.31ppm. On the other hand, the intense peak around 3.33 ppm is related to asymmetric protons of PEG. The ^{13}C spectrum was readily analyzed as well. The carbon of the Cp appears at 79.60 ppm, the complexed aromatic carbons appear as four distinct signals in the range between 78.02 to 88.78ppm. The 4,4-bis(4-hydroxyphenyl) valeric acid's aromatic carbon presents as two symmetric signals at 120.50 and 130.04 ppm. The high field quaternary carbon appearing at 147.15 and 152.09ppm for the oxygen bonded carbon and the quaternary presents is present 97.77 ppm is a consequence of the C-Cl bond of the complex's aromatic ring. Finally, the carbons of PEG show up at the range 60.00-75.00 ppm respectively.



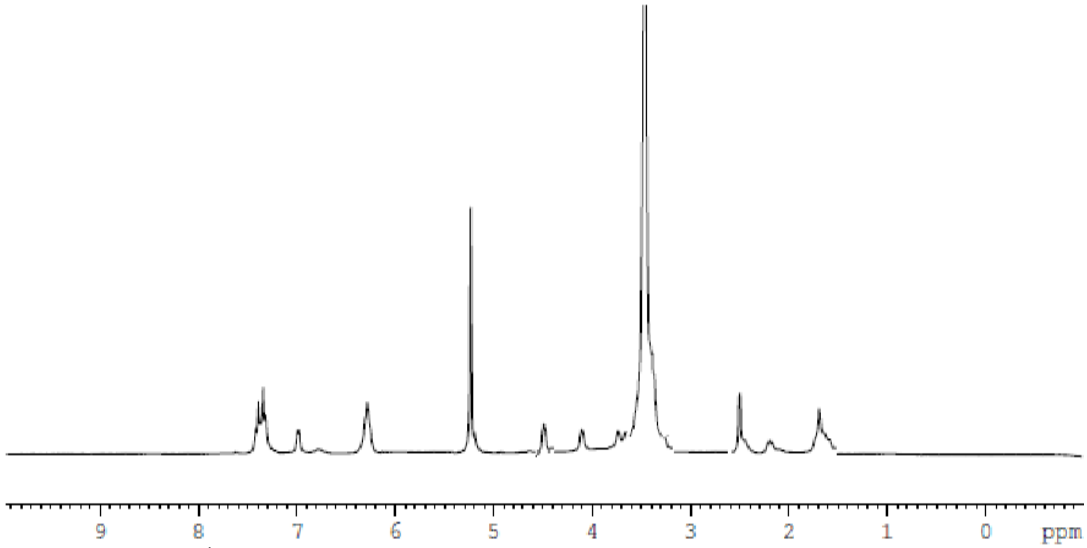


Figure 2.27: ^{1}H NMR of complex **2.16** in DMSO-d_6**.**

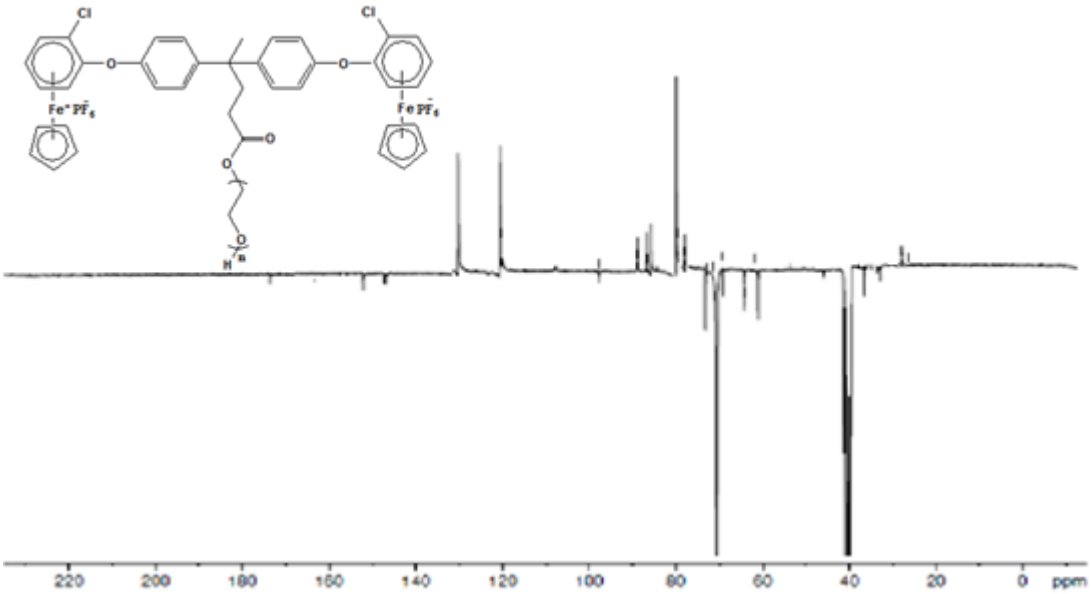


Figure 2.28: ^{13}C NMR of complex **2.16** in DMSO-d_6**.**

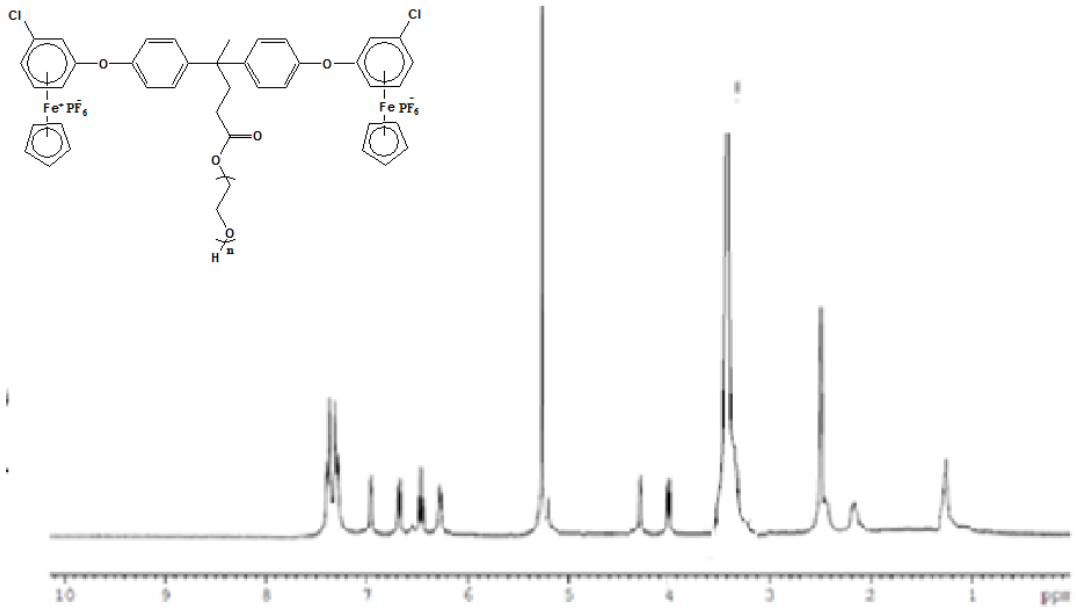


Figure 2.29: ^{1}H-NMR of complex **2.17** in DMSO-d_6**.**

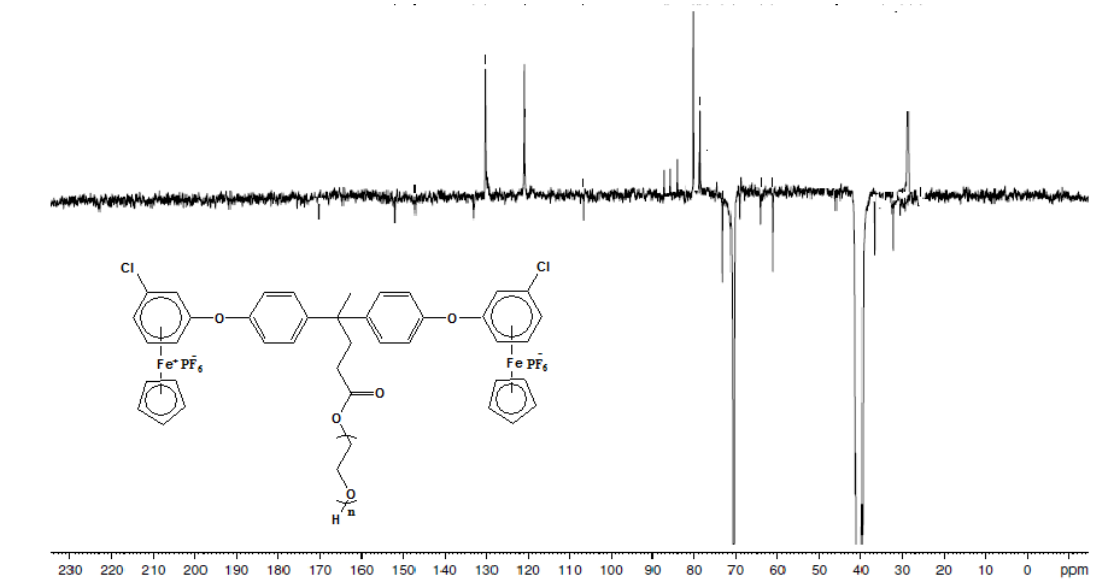


Figure 2.30: ^{13}C NMR of complex **2.17** in DMSO-d_6**.**

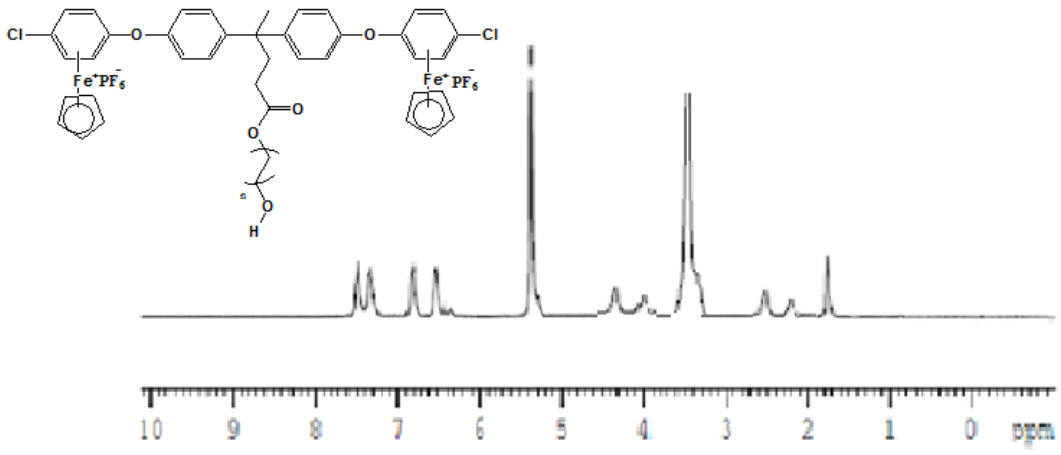


Figure 2.31: ^{1}H NMR of complex **2.18** in DMSO-d_6**.**

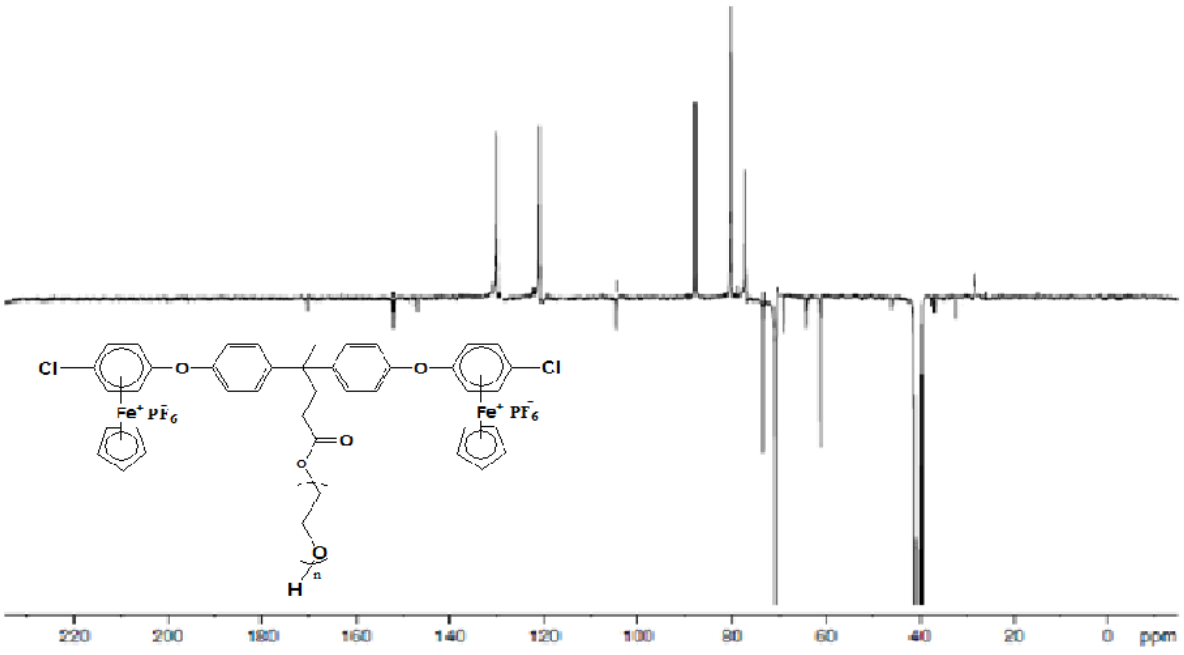


Figure 2.32: ^{13}C NMR of complex **2.18** in DMSO-d_6**.**

Table 4.01: ^{13}C NMR and ^{1}H NMR of complexes **4.01-4.03** in DMSO d_6.

Compound	Cp (ppm)	complexed aromatic (ppm)	uncomplexed aromatic (ppm)	Others (ppm)
2.16 ^{1}H	5.23(S, 10H)	6.28(S, 4H) 6.90(S, 4H)	7.31(D, 8H)	1.60(S, 3H) 2.00(S, 2H) 2.50(S, 2H) 3.33(S, 2H) 4.12(S.2H) 4.6 (S.2H)
2.16 ^{13}C	79.60	78.023 84.80 86.54 88.88 97.77	120.49 130.03 147.15 152.09	31.41 27.50 43.52 64.19 61.89 69.46 71.43 73.08 173.82
2.17 ^{1}H	5.24(S, 10)	6.30(S.1H) 6.50 (S, 1H) 6.80(S, 1H) 6.94(S, 1H)	7.30(D, 8H)	1.60(S, 3H) 2.00(S, 2H) 2.50(S, 2H) 3.30(S, 2H) 4.20(S, 2H) 4.40(S, 1H
2.17 ^{13}C	79.09	77.85 86.31 86.90 106.45	120.90 130.19 152.01 157.16	31.50 38.12 41.34 63.98 61.51 70.60 73.20 76.90 172.33
2.18 ^{1}H	5.23(S, 10H)	6.40(D, 4H) 6.70(D, 4H)	7.33(S, 8H)	1,60(S, 3H) 1.98 (S, 2H) 2.45(S, 2H) 3.41(S, 2H) 4.07(S, 2H) 4.75(S, 2H)
2.18 ^{13}C	80.32	87.50 77.31 104.36 131.92	121.12 129.08 133.01 147.22 152.99	26.97 31.27 36.80 45.09 60.24 63.97 68.80 70.78 73.05 77.36

2.2.3.4 - Thermal Properties of the compound

The thermal properties of the 4.03 complex with cationic organoiron moieties were studied using thermogravimetric analysis (TGA). The complex containing cyclopentadienyliron cations coordinated to arenes in their backbones underwent two weight loss steps. The first degradation (17 to 33 %) occurs between 219 and 260 ^{0}C correspondsto the loss of the pendent iron complexes. Additional weight loss steps were observed starting at 390 °C and attributed to the backbone degradation of the complex.

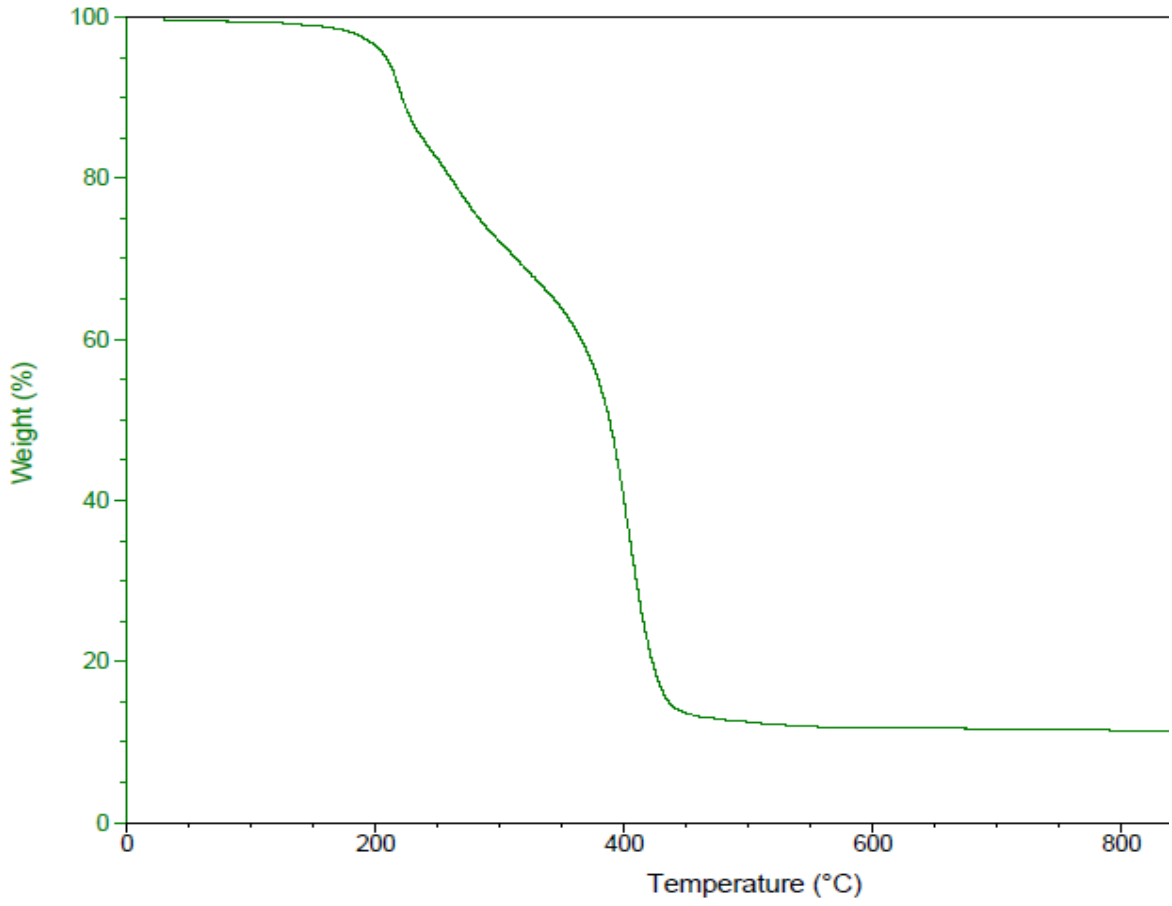


Figure 2.27: TGA Thermogram of compound **4.02** in Nitrogen**.**

Chapter 3: Synthesis of Polyaromatic Ethers.

3.1 Introduction.

It has been demonstrated that nucleophilic aromatic substitution of haloarenes complexed to transition metal moieties with oxygen-, sulfur-, and nitrogen- containing nucleophiles facilitate the synthesis of a wide variety of aryl ether thioethers and amines. These metaled-mediated reactions proceeded under very mild conditions and facilitate the incorporation of some different functional groups. Nucleophilic substitution reactions of chloroarenes complexed to the cyclopentadienyliron moieties have been the subject of many studies directed towards the design of functionalized monomers.

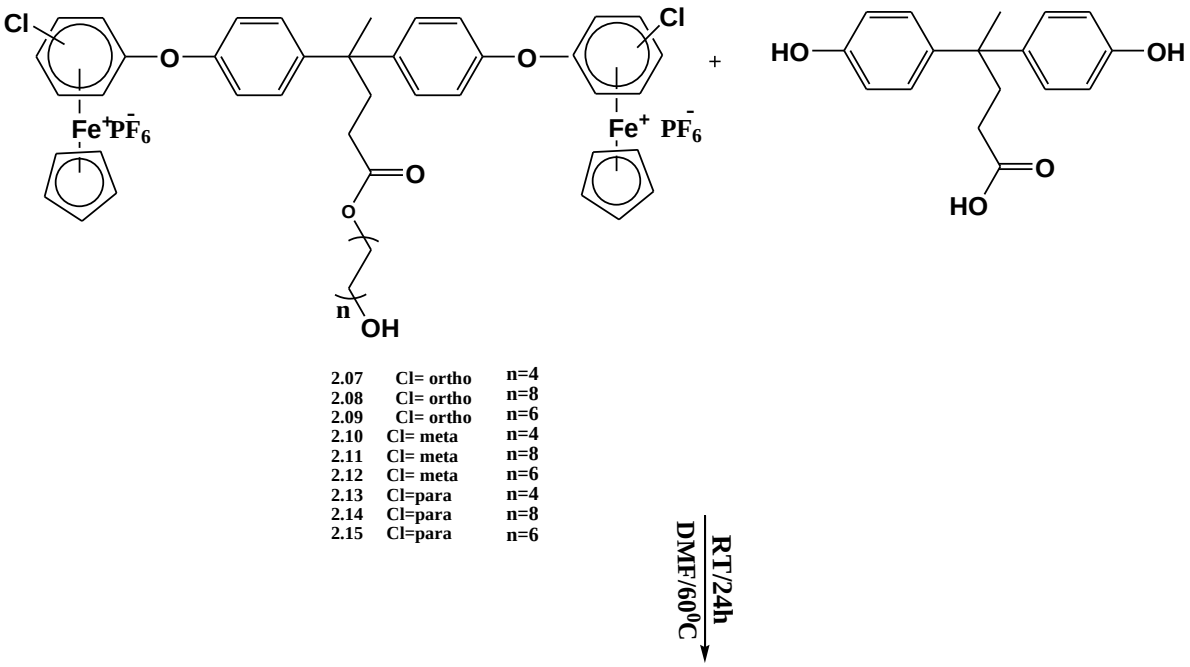
There have been only a few publications on the synthesis of polymers containing metal moieties π-coordinated to phenylene units in the polymer backbone. The metallic groups have included chromium tricarbonyl, molybdenum tricarbonyl, manganese tricarbonyl, cyclopentadienyliron, cyclopentadienyl ruthenium, and pentamethylcyclopentadienyl ruthenium. These organometallic polymers have demonstrated interesting electrochemical and liquid crystalline properties. Some studies have shown that the incorporation of metallic moieties pendent to polymeric materials resulted in enhanced solubilities of the organometallic polymers. Various approaches to

the synthesis of this class of polymer have been taken advantage of. One method involves the coordination of a metallic moiety to an organic polymer via a ligand exchange reaction. This methodology has been utilized in the production of polymers with $Cr(CO)_3$, $Mo(CO)_3$ and CpFe*moieties pendent to aromatic rings in the polymer backbone. Another method that has been implemented in the synthesis of η^6-complexed organometallic polymers involves polycondensation reactions of π-coordinated organometallic monomers. The supramolecular assembly of arene complexes has also recently been described. The final approach is via nucleophilic aromatic substitution reactions mediated by the transition metal moiety. This work illustrates the synthesis and characterization of polyaromatic ethers coordinated to cyclopentadienyliron cation via nucleophilic aromatic substitution reactions.

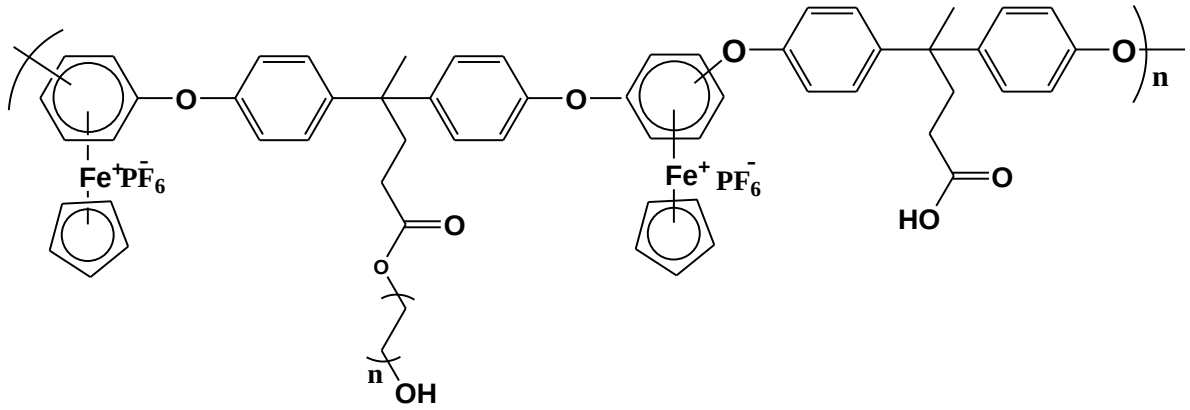
3.2 Results and Discussion

3.2.1 Synthesis of Polyaromatic Ether Coordinated to Cationic cyclopentadienyliron Moieties.

It was well established that the type of aromatic linkage incorporated into polyaromatic ethers has a strong impact on the thermal and physical properties of these materials. Therefore, the organoiron polymers demonstrated in Scheme 3.01 were prepared by the reaction of isomeric-dichlorobenzene complexes containing different lengths of the aliphatic alcohol with 4,4- Bis (4-hydroxyphenyl) valeric acid in the presence of DMF as a solvent and K_2CO_3 as a base to test the solubility of these compounds. These reactions allowed for the formation of polyaromatic ether containing pendent cyclopentadienyliron moieties in yields ranging from 89 to 99%. Typically, this class of polymer is synthesized at high temperature and in the presence of strong electron withdrawing group. However, the presence of the electron-withdrawing cyclopentadienyliron moiety pendent to the dichloroarene allows these polymerization reactions to take place at 60 $^{\circ}$C over a period of 24 hours.



2.07	**Cl= ortho**	**n=4**
2.08	**Cl= ortho**	**n=8**
2.09	**Cl= ortho**	**n=6**
2.10	**Cl= meta**	**n=4**
2.11	**Cl= meta**	**n=8**
2.12	**Cl= meta**	**n=6**
2.13	**Cl=para**	**n=4**
2.14	**Cl=para**	**n=8**
2.15	**Cl=para**	**n=6**



3.01	O= ortho	n=2
3.02	O= ortho	n=4
3.03	O= ortho	n=6
3.04	O= meta	n=2
3.05	O= meta	n=4
3.06	O= meta	n=6
3.07	O=para	n=2
3.08	O=para	n=4
3.09	O=para	n=6

Scheme 3.01: Synthesis of Complexes **3.01-3.06**.

It was found that the length of aliphatic alcohol affects the solubility of the polymers; the length increases, so does the solubility of the polymers. It was known that the inherent poor solubility of rigid aromatic molecules such as compound **3.01** decrease the ability to prepare these types of polymers. However, the insoluble polyaromatic ether makes them valuable for certain applications where these materials need to maintain their chemical resistance over a long period.

^{1}H and ^{13}C NMR analysis of the cyclopentadienyliron -coordinated polyaromatic ether are very powerful tools in order to examine the polymerization reactions. The ^{1}H NMR spectrum of the **2.07** is straightforward, with cyclopentadienyl resonance displayed as a singlet at 5.27 ppm. Upon polymerization, the resonance corresponding to this peak underwent upfield shift. The appearance of one singlet representing the cyclopentadienyliron protons in the polymers spectra at 5.22 ppm indicated that there was no starting complex remaining. Furthermore, the complexed aromatic protons were shifted upfield in polymers **3.01-3.09** to 6.20-6.55 ppm while the uncomplexed aromatic ethers appear at 6.80 ppm. Particularly, the appearance of the Cp complexes **3.01-3.09** with etheric bridges indicated successful polymer preparation. Additionally, the presence of one complexed aromatic resonance

(CH) appeared at 84.60 ppm for the polymer **3.01**, whereas the polymers **3.07** appear at 76.04 ppm.

Figure 3.03 represents ^{1}H NMR spectrum of the polymer **3.02** The twenty-eight protons of the aliphatic groups appear to overlap in the range between 1.30 ppm – 2.50 ppm. The four protons, related to the carbons close to ester or alcohol, appear at 3.95 ppm and 4.43 ppm respectively. It has been seen that the five- cyclopentadienyliron protons as appear as a signal peak shifted upfield at 5.19ppm, and the four complexed aromatic protons have shifted and appeared at 6.06, 6.40 and 6.77ppm. Lastly, the protons corresponding to the bridging aromatic rings appear in the region of 7.10ppm.

In the ^{13}C NMR spectrum of polymer **3.02**, the sixteen aliphatic carbons appear in the range of 23.00 to 42.00 ppm, and the two carbons close to ester and alcohol groups appear at 61.50 and 64.53 ppm respectively. The cyclopentadienyliron resonance appears at 78.88 ppm as an intense peak pointing up. The complexed aromatic CH carbons appear at 84.20 ppm, while the quaternary complexed aromatic carbons appear at 125.34 ppm. The four uncomplexed aromatic peaks appear further upshifted to 115.50, 120.49, 128.70 and 130.13 ppm. The ^{1}H NMR and ^{13}C NMR of polymers are given in Table 3.01 and 3.02.

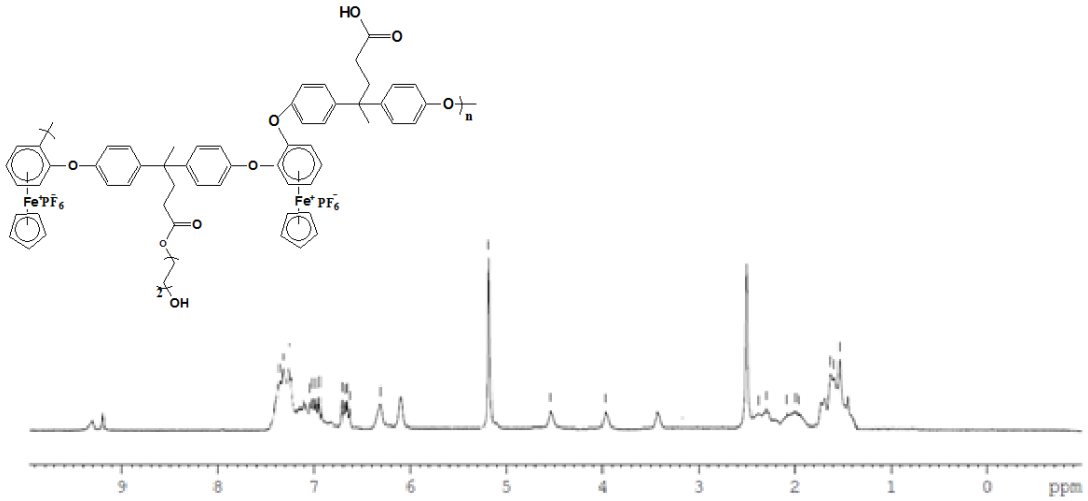


Figure 3.01: ^{1}H NMR of complex **3.01** in DMSO-d_6**.**

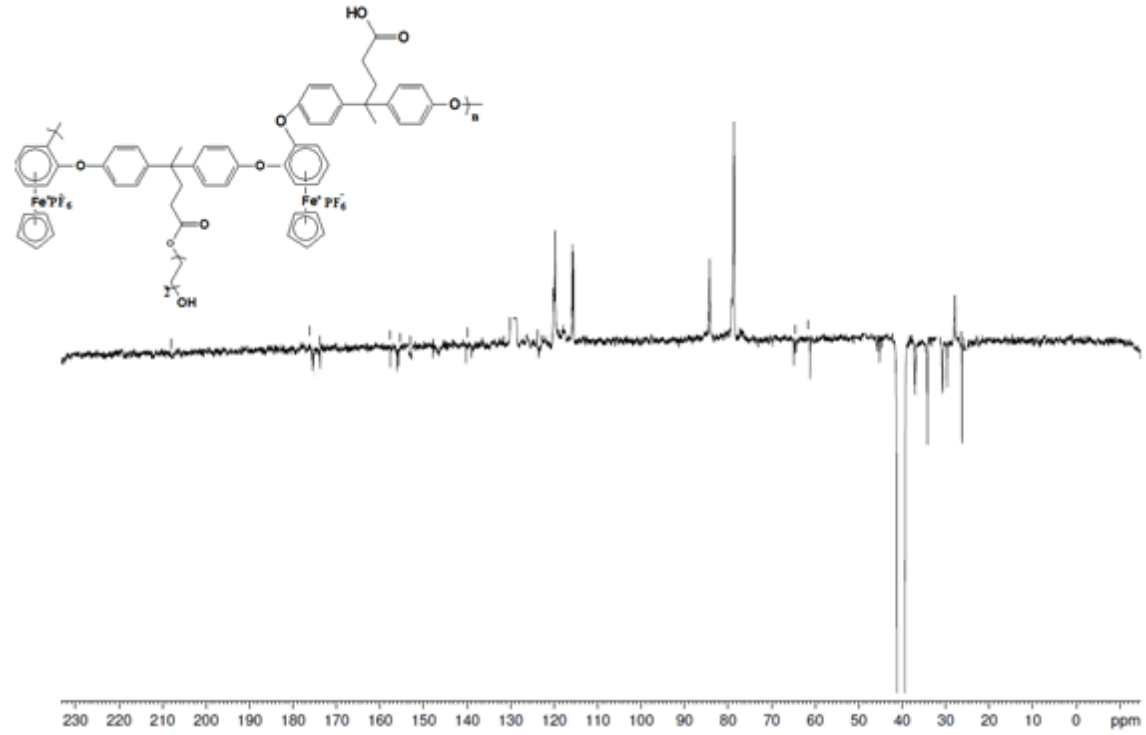


Figure 3.02: ^{13}C NMR of complex **3.01** in DMSO-d_6**.**

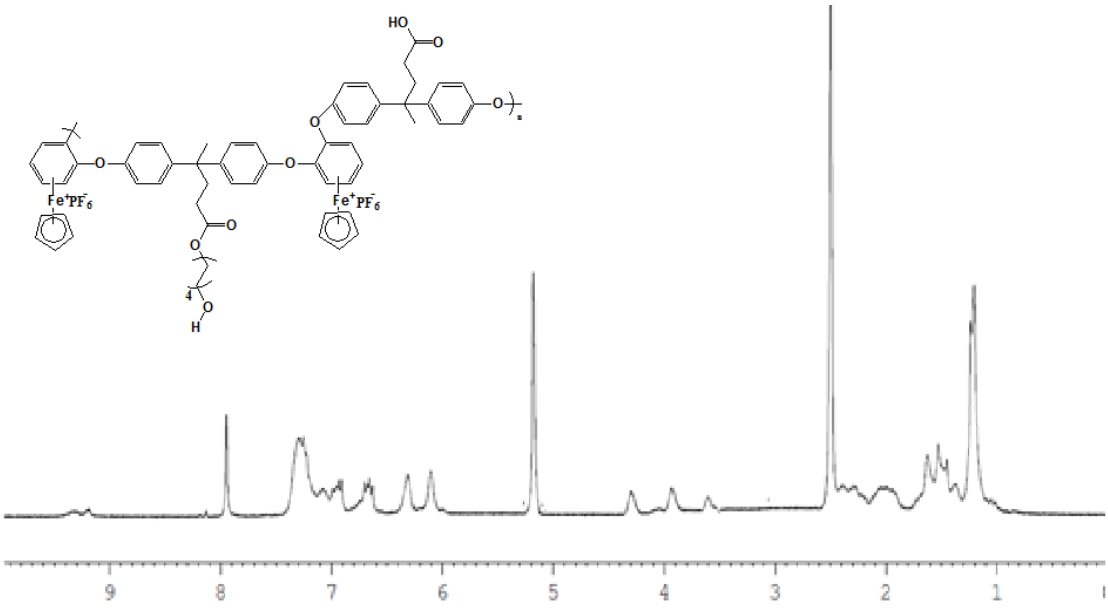


Figure 3.03: ^{1}H NMR of complex **3.02** in DMSO-d_6**.**

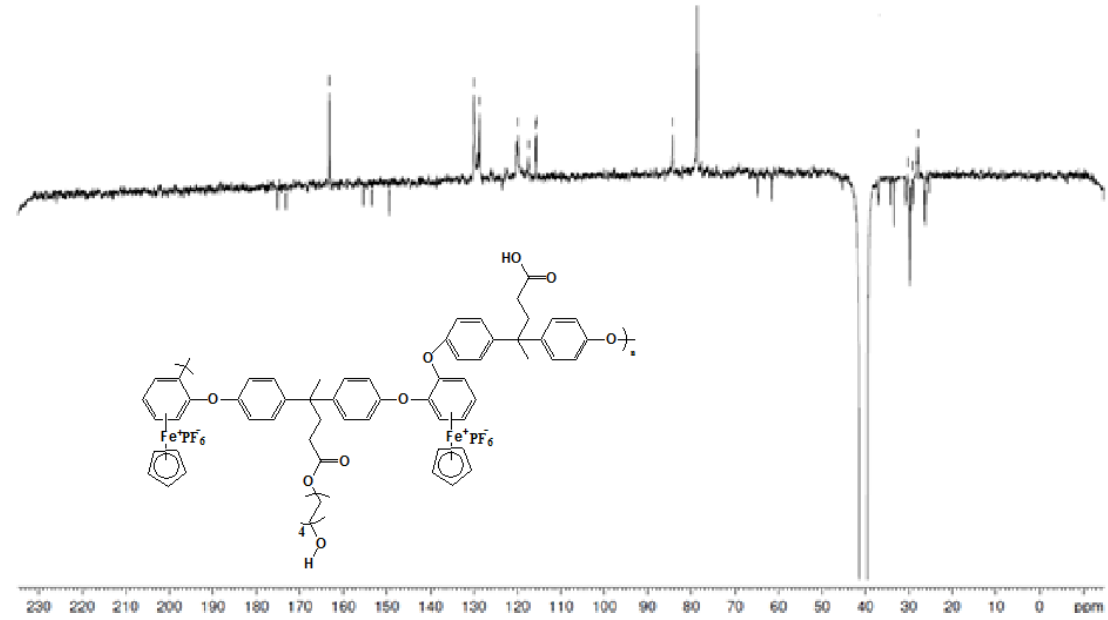


Figure 3.04: ^{13}C NMR of complex **3.02** in DMSO-d_6**.**

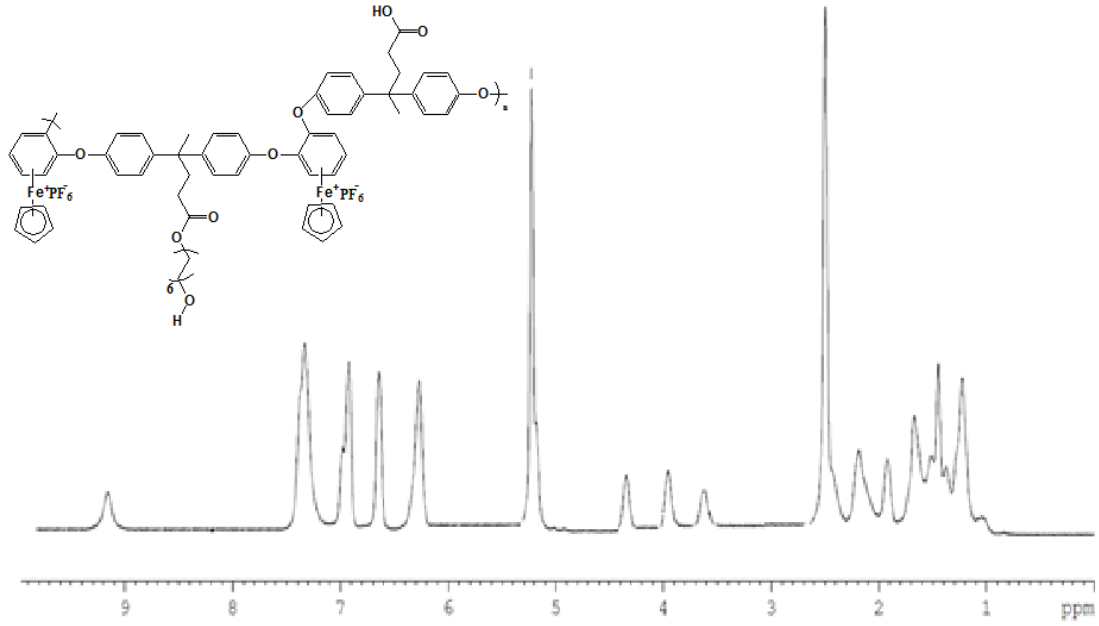


Figure 3.05: ^{1}H NMR of complex **3.03** in DMSO-d_6**.**

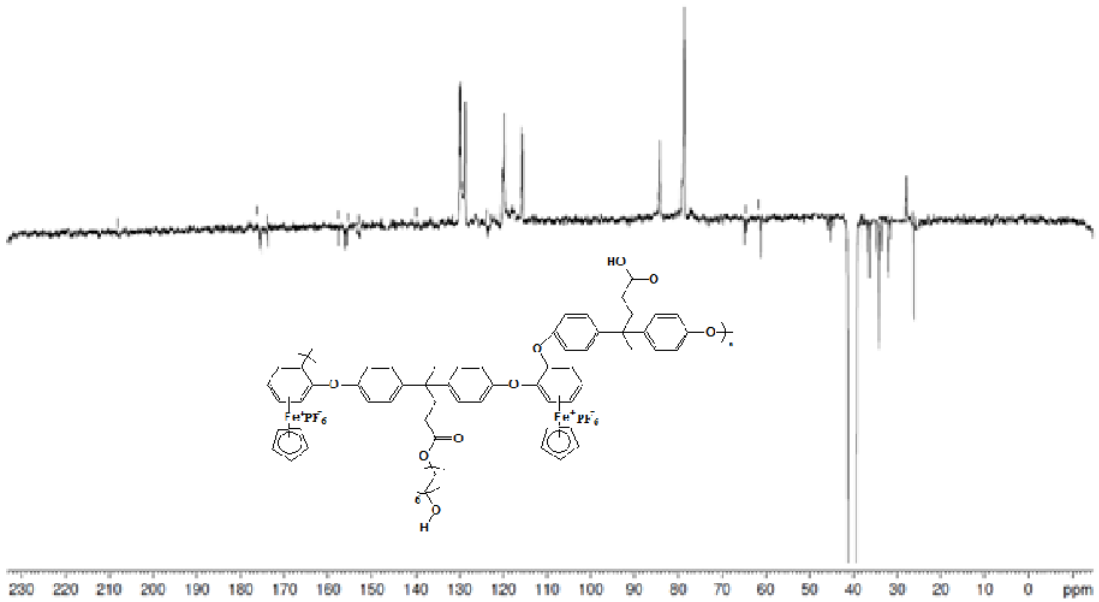


Figure 3.06: ^{13}C NMR of complex **3.03** in DMSO-d_6**.**

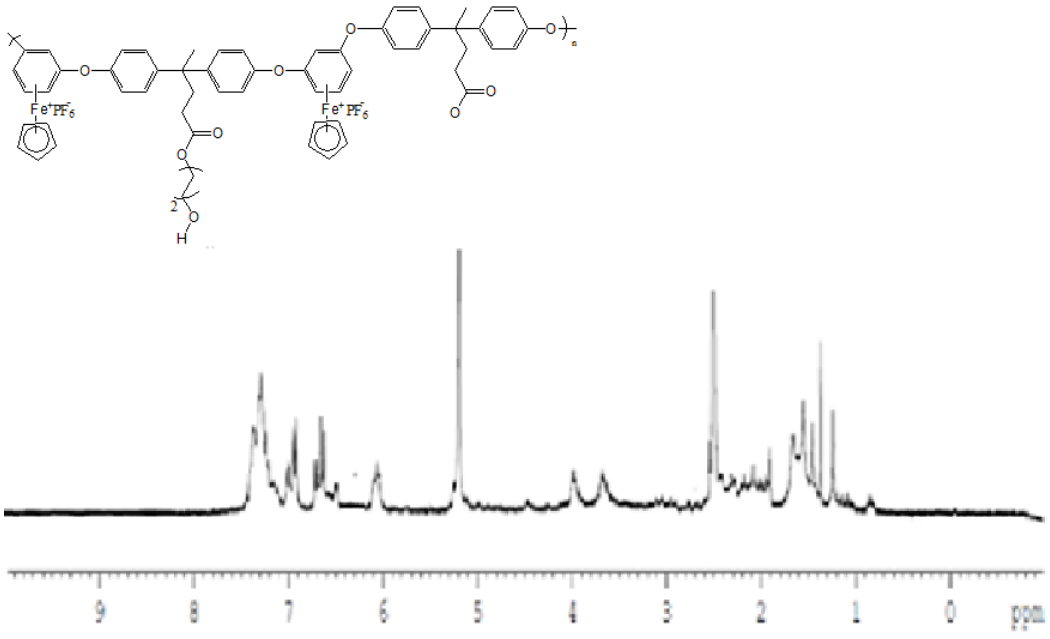


Figure 3.7: ^{1}H NMR of complex **3.04** in DMSO-d_6**.**

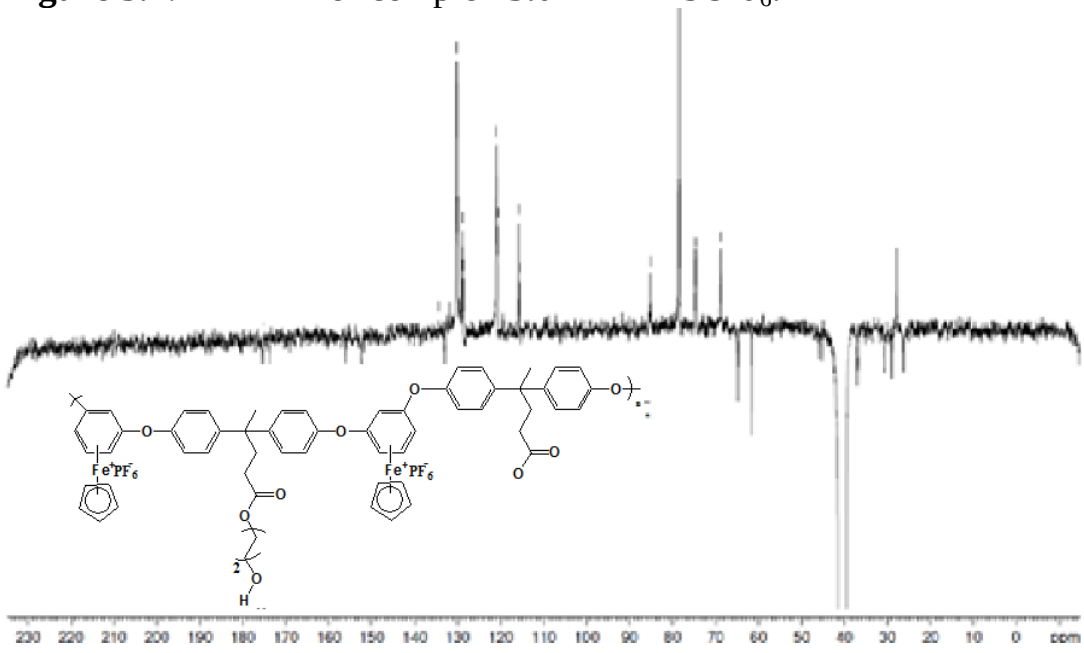


Figure 3.08: ^{13}C NMR of complex **3.04** in DMSO-d_6**.**

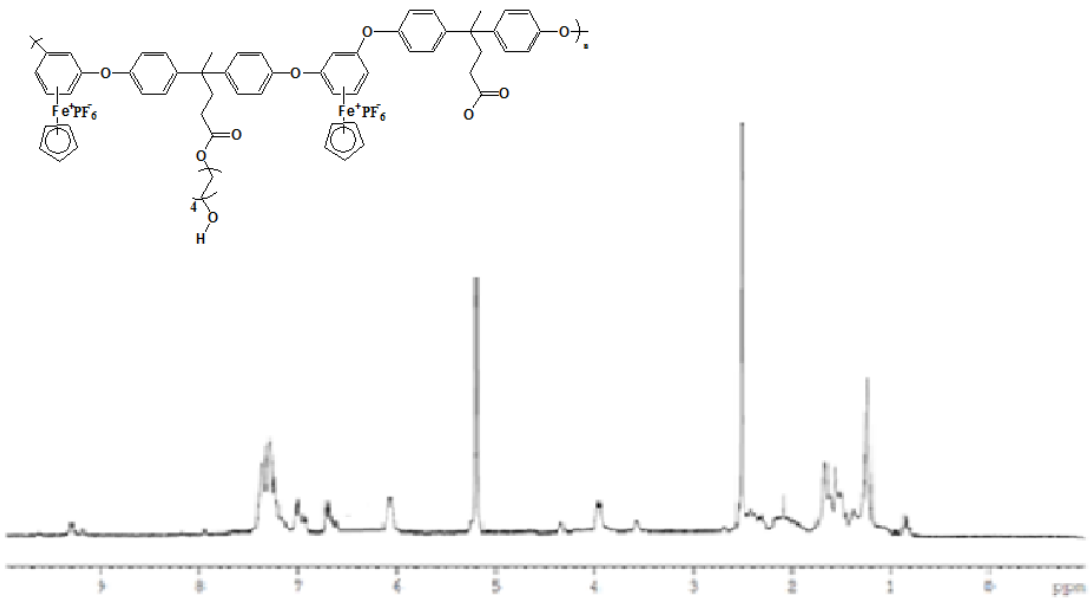


Figure 3.09: ^{13}C NMR of complex **3.05** in DMSO-d_6**.**

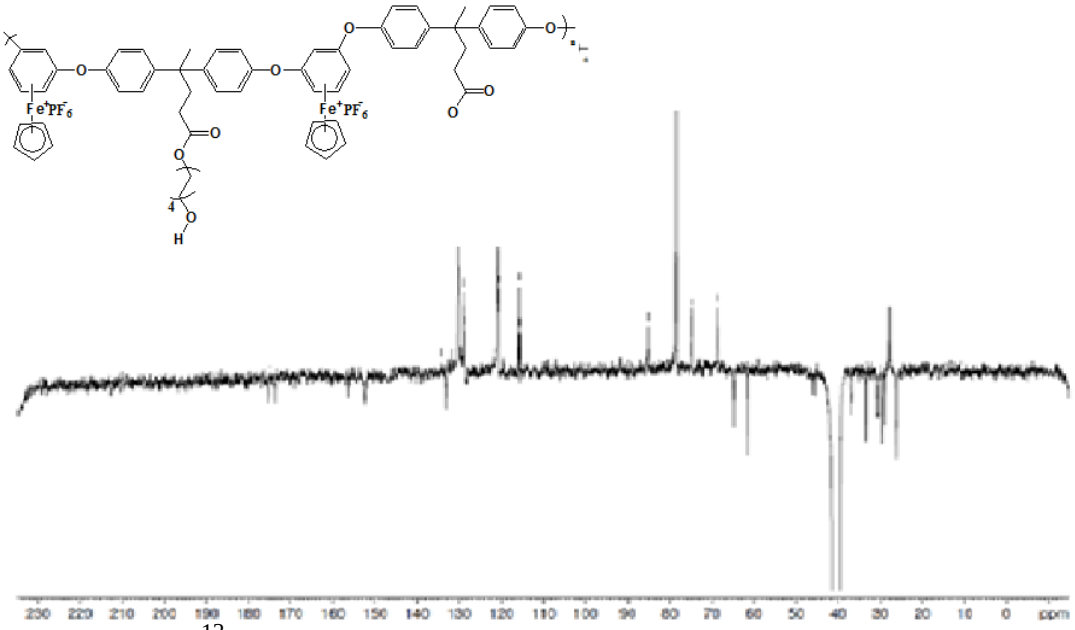


Figure 3.10: ^{13}C NMR of complex **3.05** in DMSO-d_6**.**

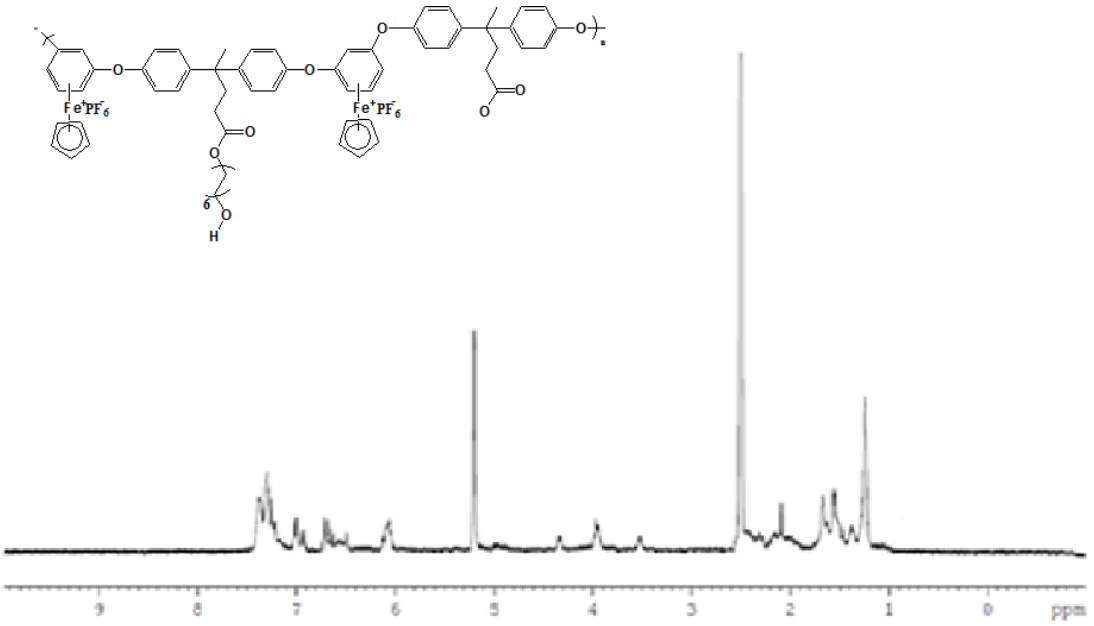


Figure 3.11: ^{1}H NMR of complex **3.06** in DMSO-d_6**.**

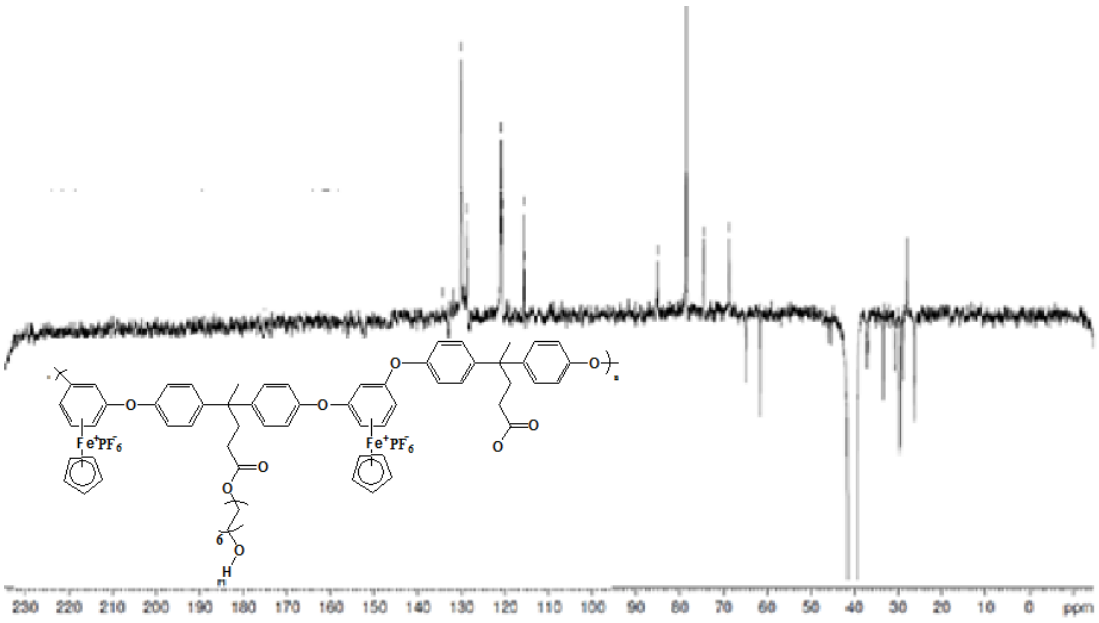


Figure 3.12: ^{13}C NMR of complex **3.06** in DMSO-d_6**.**

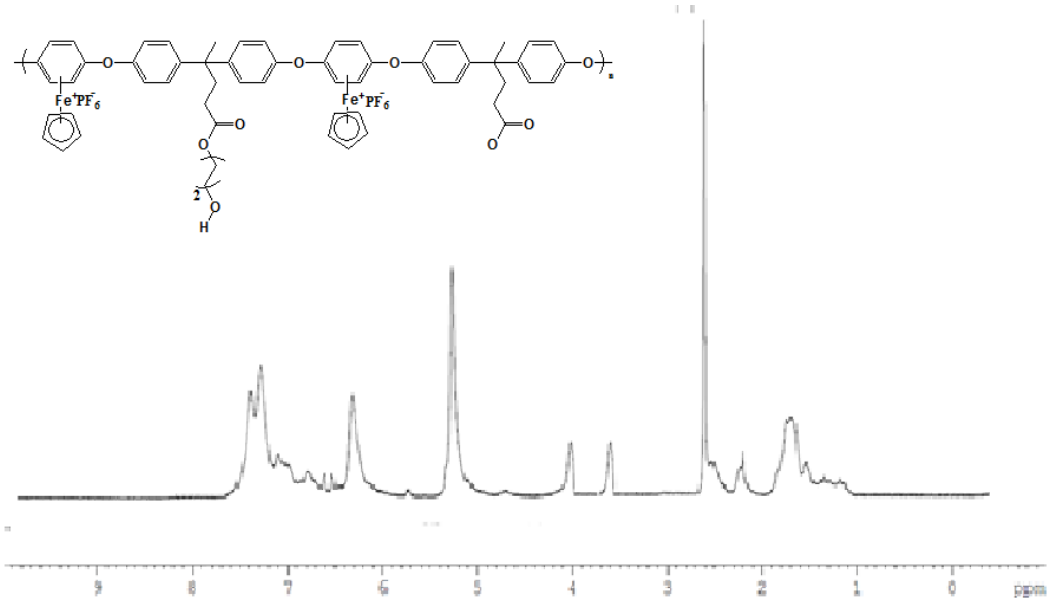


Figure 3.13: ^{1}H NMR of complex **3.07** in DMSO-d_6**.**

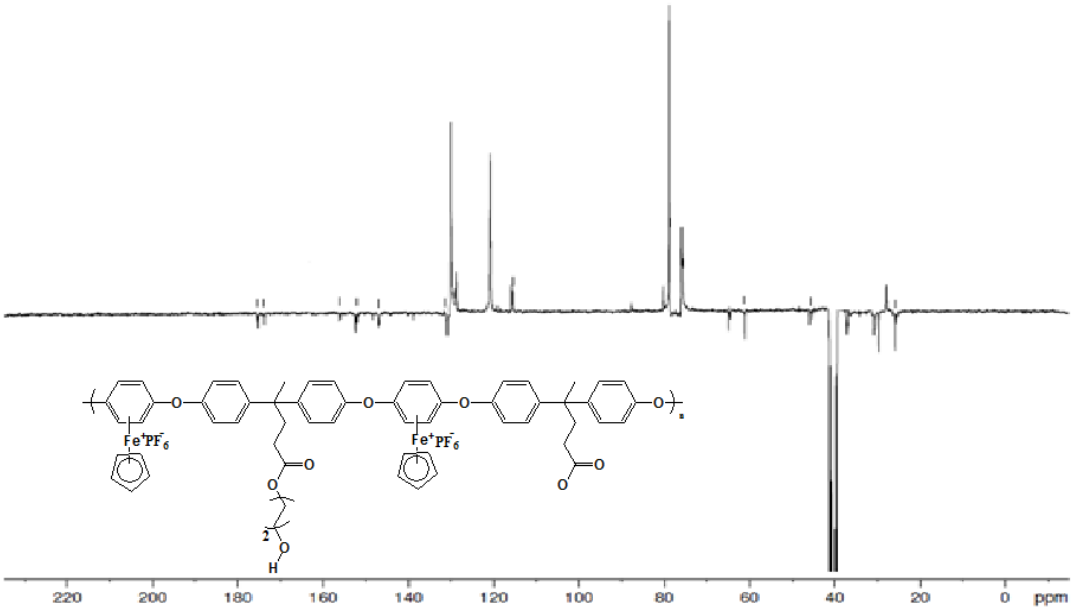


Figure 3.14: ^{13}C NMR of complex **3.07** in DMSO-d_6**.**

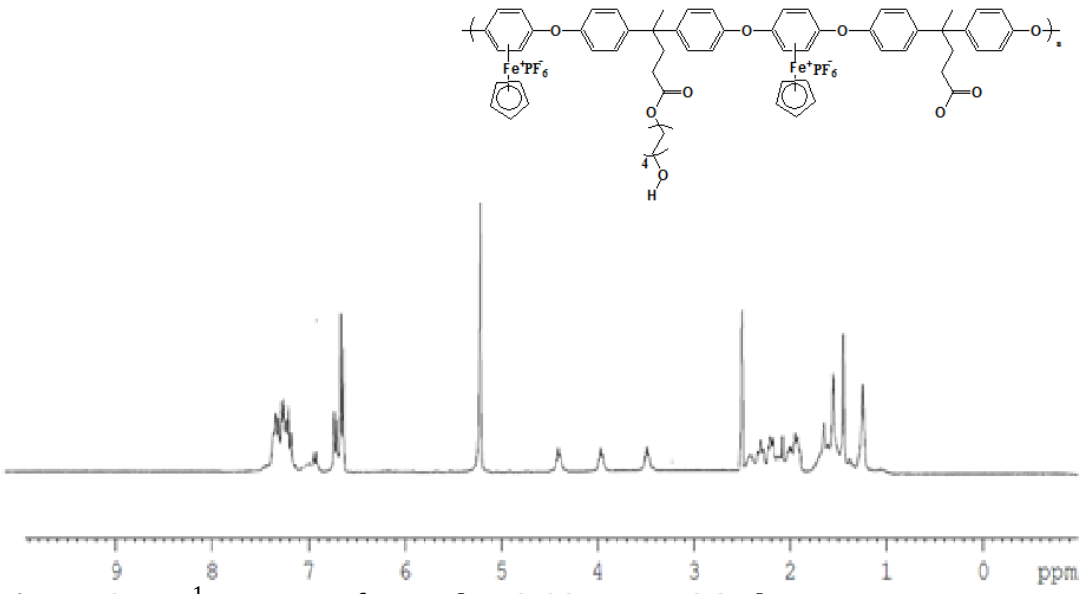


Figure 3.15: ^{1}H NMR of complex **3.08** in DMSO-d_6**.**

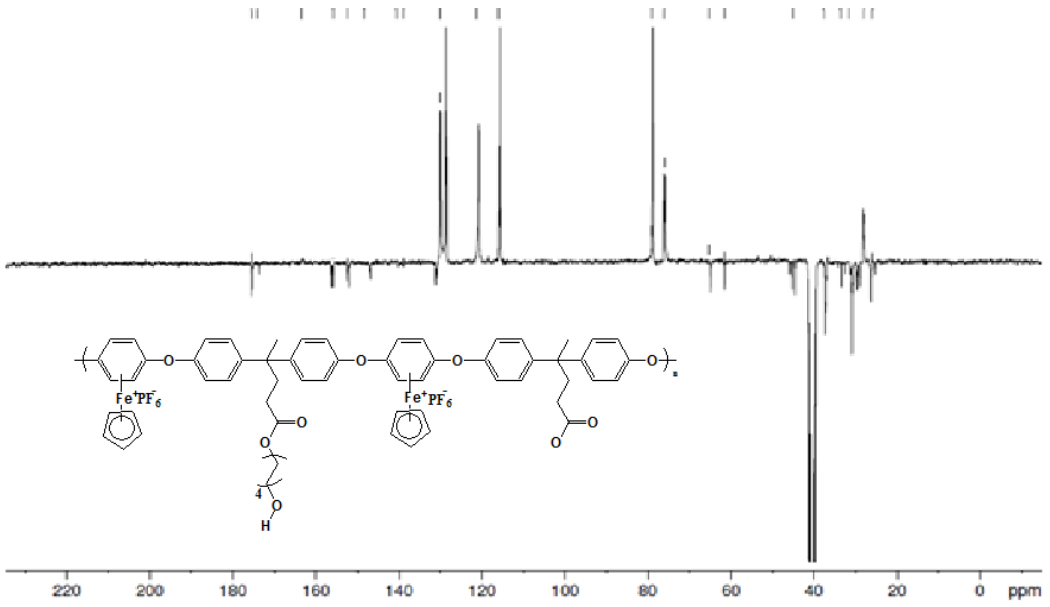


Figure 3.16: ^{13}C NMR of complex **3.08** in DMSO-d_6**.**

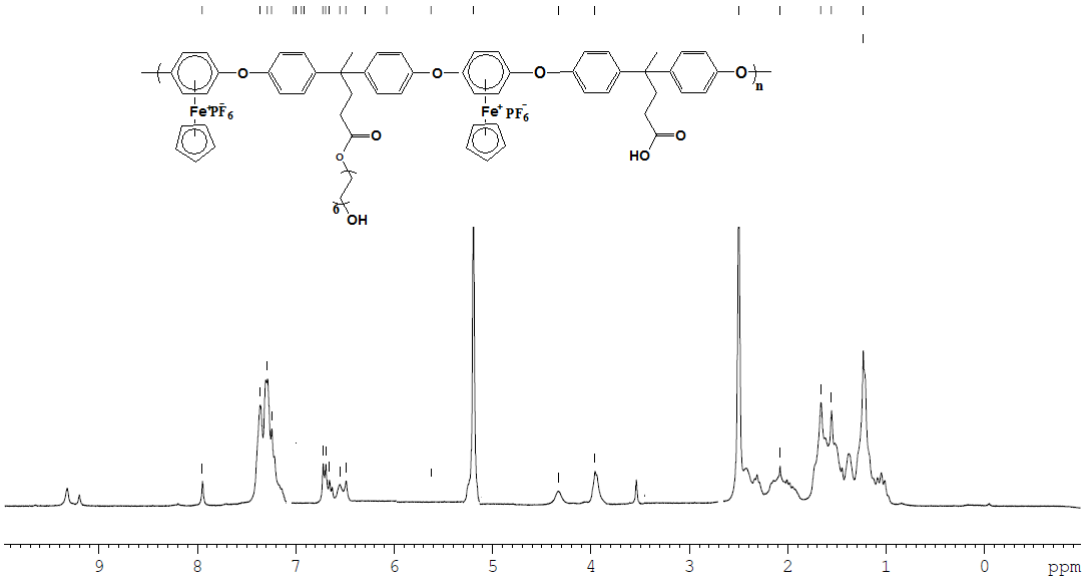


Figure 3.17: ^{1}H NMR of complex **3.09** in DMSO-d_6**.**

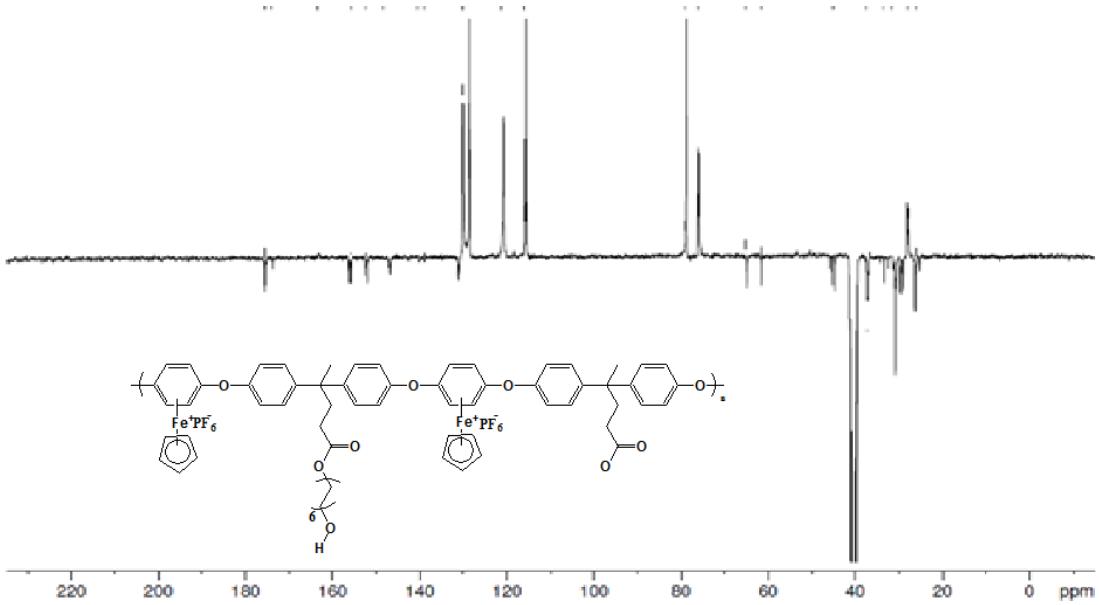


Figure 3.18: ^{13}C NMR of complex **3.09** in DMSO-d_6**.**

Table 3.01: ^{1}H NMR analysis of complexes **3.01-3.06** in DMSO d_6

Compound	Cp	Complexed aromatic	Uncomplexed Aromatic	Others
3.01 ^{1}H	5.18(S, 5H)	6.10(S,1H,) 6.50 (S, 1H) 6.87 (S, 2H)	7.37(S,8H)	1.26-1.78(M,10H) 1.93(S, 4H) 2.50(S, 4H) 3.50(S,2H) 3.95(S,2H) 4.50 (S.1H)
3.02 ^{1}H	5.19(S,5H)	6.10 (S,1H,) 6.40 (S, 1H) 6.77 (S,2H)	7.10 (M,8H)	1.30-1.76(M,18H) 1.93(S,4H) 2.2(S,4H) 3.45(S,2H) 3.95(S,2H) 4.43 (S.1H)
3.03 ^{1}H	5.21(S,5H)	6.10(S,1H,) 6.43 (S, 1H) 6.77(S, 2H)	7.11 (M,8H)	1.22-1.76(M,26H) 1.93(S,4H) 2.28(S,4H) 3.45(S,2H) 3.95(S,2H) 4.47 (S.1H)
3.04 ^{1}H	5.18(S, 5H)	6.10(S,1H,) 6.20 (S, 1H,S) 6.80(S, 2H)	7.10(M,8H)	1.3-1.8(M,10H) 2.00(S,4H) 2.5(S, 4H) 3.5(S, 2H) 3.95(S, 2H) 4.50 (S.1H)
3.05 ^{1}H	5.19(S, 5H)	6.06(S,1H) 6.40 (S, 1H,S) 6.80(S, 2H)	7.07 (M,8H)	1.3-1.8(M,18H) 1.95(S, 4H) 2.5(S, 4H) 3.5(S, 2H) 3.95(S, 2H) 4.5 (S.1H)
3.06 ^{1}H	5.19(S, 5H)	6.10(S,1H,) 6.50 (S, 1H) 6.87(S, 2H)	7.14(M,8H)	1.30-1.80(M,26H) 1.95(S, 4H) 2.5(S, 4H) 3.5(S, 2H) 3.95(S, 2H) 4.50 (S.1H)
3.07 ^{1}H	5.19(S, 5H)	6.20(S, 2H)	7.20(M, 8H)	1.20-1.80(M, 10H) 2.1(S, 4H)

				2.5(S, 4H) 3.5(S, 1H) 3.95(S, 2H) 4.5 (S,2H)
3.08 ^{1}H	5.19(S, 5H)	6.20(S, 2H)	7.20(M, 8H)	1.2-1.8(M, 18H) 2.32(S, 4H) 2.6(S, 4H) 3.44(S, 2H) 3.97(S, 2H) 4.25 (S.1H)
3.09 ^{1}H	5.19(S, 5H)	6.20(S, 2H)	7.20(M, 8H)	1.2-1.8(M, 28H) 2.32(S, 4H) 2.6(S, 4H) 3.44(S, 2H) 3.97(S, 2H) 4.25 (S.1H)

Table 3.02: ^{13}C NMR Analysis of Complexes 3.01-3.06 in DMSO d_6

Compound	Cp	Complexed aromatic	Uncomplexed Aromatic	Others
3.01 ^{13}C	78.68	84.60 138.00 147.70	115.88 120.2 128.75 130.03 139.9 155.38 157.69	26.33 27.9 29.8 31.9 37.2 45.43 61.5 64.52 173.8 176.15
3.02 ^{13}C	78.88	84.20 138.32 147.46	116.13 120.20 128.70 130.13 139.90 155.24 157.66	26.44 27.22 27.80 33.90 38.20 44.94 61.50 64.52 173.8 176.14
3.02 ^{13}C	78.93	84.33 138.41 147.10	115.88 120.20 128.70 130.03 139.90 155.38	26.33 27.90 29.8 31.90 37.20 45.43 61.50 64.52 173.8 176.12

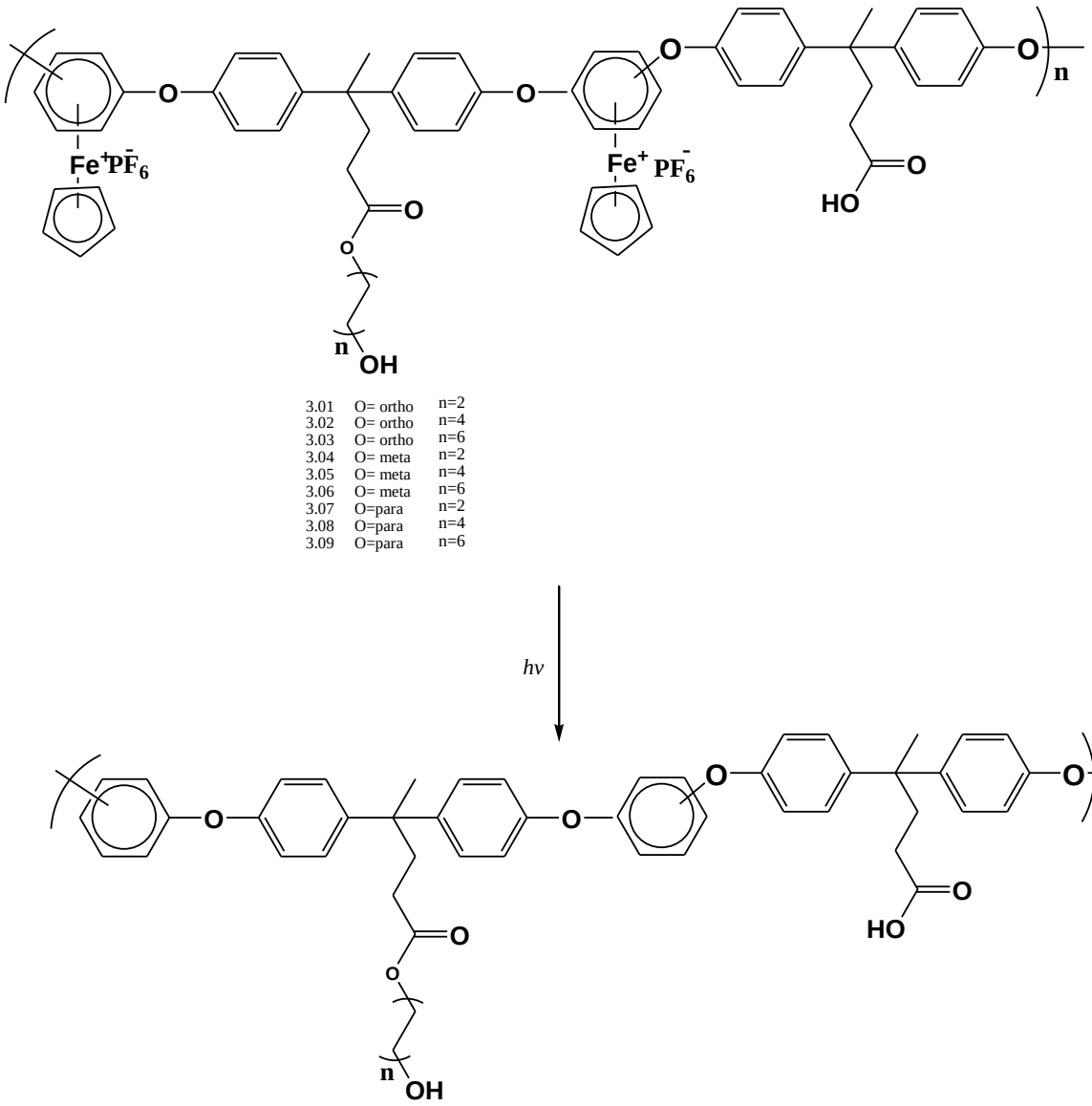
			157.69	
3.04 ^{13}C	78.92	74.54 85.53 68.30 133.09 147.23	117.12 122.32 128.78 130.70 153.40 156.80	26.5 27.40 33.90 38.20 44.94 61.50 64.52 173.8 175.13
3.05 ^{13}C	78.60	74.50 85.22 68.90 133.13 147.13	116.70 121.09 128.78 130.70 152.50 156.80	26.44 27.22 28.30 33.90 38.20 44.94 61.5 64.52 173.80 176.12
3.06 ^{13}C	78.75	74.47 85.53 68.5 133.17 147.23	119.12 124.32 130.78 130.70 153.21 155.76	26.34 22.98 28.3 33.9 39.2 44.94 61.4 64.7 173.8 175.93
3.07 ^{13}C	79.01	76.04 131.82 148.14	115.80 121.15 130.00 131.00 152.42 156.71	27.98 31.60 31.60 37.53 61.56 65.18 174.15 175.47
3.08 ^{13}C	78.68	75.04 131.82 148.149	114.77 120.23 130.00 131.00 152.42 156.71	26.08 27.90 29.50 31.55 37.53 45.10 61.56 65.18 174.15 175.47
3.09 ^{13}C	78.68	75.24 131.32 148.29	116.77 122.23 131.20 131.00 154.52 156.71	26.08 27.22 29.33 31.35 37.53 45.22 61.43 65.18 174.23 175.34

3.3 Removal of Organic Polymers by Photolytic Demetallation

Segal and Dembek have demonstrated that the determination of the degree of polymerization of this class of organometallic polymers utilizing Gel Permeation Chromatography (GPC) is difficult because of the tendency of the cationic metallic moieties pendent to the polymeric chains to interact with the GPC column[58,119]. In light of this investigation, successful removal of the iron moieties from the backbone of these materials facilitated the determination of the degree of polymerization.

The relatively weak coordination bonds between the cyclopentadienyliron and the arene ring in the cationic organoiron groups can be readily removed utilizing UV light (300 nm) in a strongly coordinating solvent such as acetonitrile. Solutions of polymers **3.01-3.09** in CH_3CN were exposed to 300 nm light for 6 hours to give polymers **3.10-3.18** (Scheme 3.02). Following the appropriate work-up method, the corresponding organic polymers, **6.10- 6.18**, were isolated in approximately 35 % yields (Schemes 3.02). It is necessary to observe that upon degradation, the resulting purely organic polymers were discovered to be much less soluble in most solvents such as acetone, THF, and chloroform in comparison to their corresponding metallated materials.

^{1}H and ^{13}C NMR were used to verify the removal of the organic polymers from the corresponding metallated species (Tables 3.03 and 3.04). Table 3.03 and 3.04 illustrate the ^{1}H and ^{13}C NMR spectra of polymer **3.11** and represent the typical spectral changes observed upon liberation of the modified organic ligand from its metallic counterpart. The most notable spectral change observed upon demetallation is the disappearance of the cyclopentadienyl peaks at 5.19 ppm and 78.88 ppm in the ^{1}H and ^{13}C NMR spectra, respectively. Additionally, peaks at 6.06, 6.40 and 6.77 ppm in the ^{1}H NMR spectrum representative of the complexed aromatic protons shifted downfield to 6.90 ppm in the organic spectrum. A downfield shift of the resonances represent the complexed aromatic carbon atoms from 84.20 to 126.34 ppm and quaternary carbon resonance from 106.75 to 143.90 ppm, respectively, in the ^{13}C NMR spectrum of polymer 6.11 also support the successful cleavage of the purely organic polymer.



3.01	O= ortho	n=2
3.02	O= ortho	n=4
3.03	O= ortho	n=6
3.04	O= meta	n=2
3.05	O= meta	n=4
3.06	O= meta	n=6
3.07	O=para	n=2
3.08	O=para	n=4
3.09	O=para	n=6

Scheme 3.02 : Photolytic Demetallation of compounds **3.01**-**3.09** to form **3.10- 3.18**.

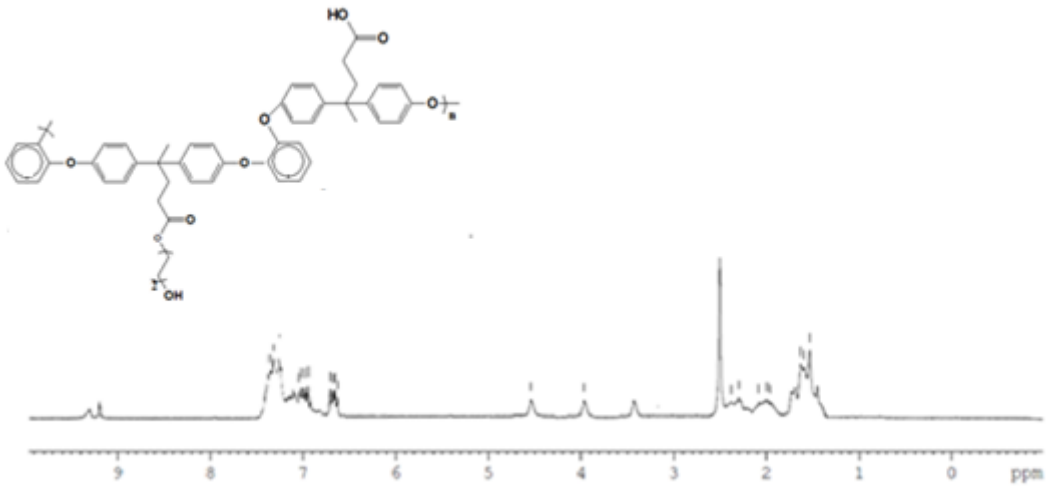


Figure 3.19: ^{1}H NMR of compound **3.10** in DMSO-d_6**.**

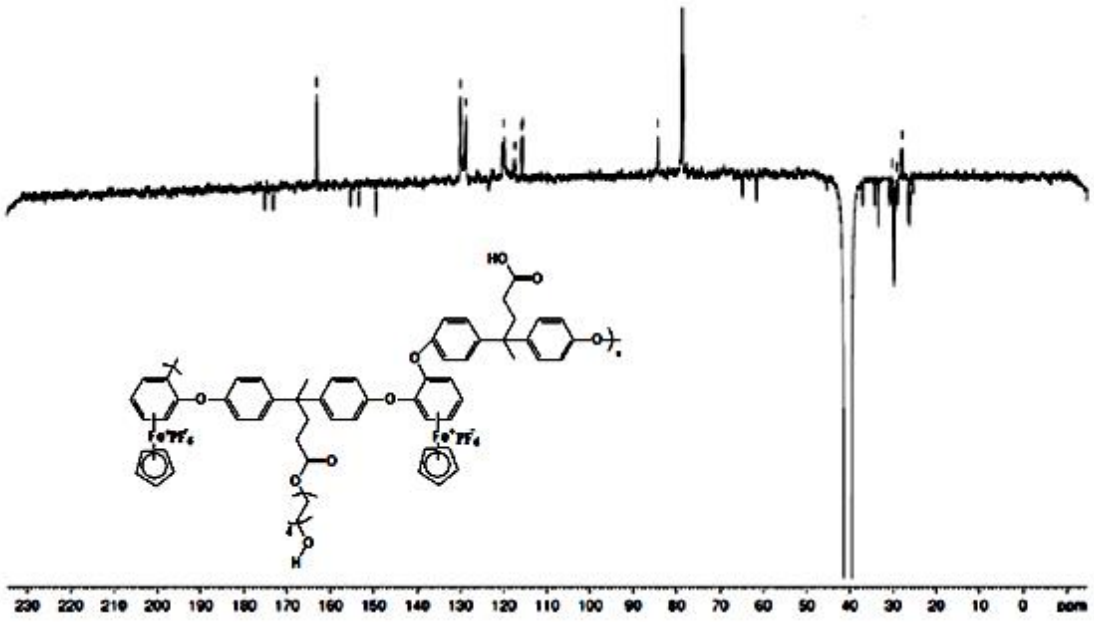


Figure 3.20: ^{13}C NMR of compound **3.10** in DMSO-d_6**.**

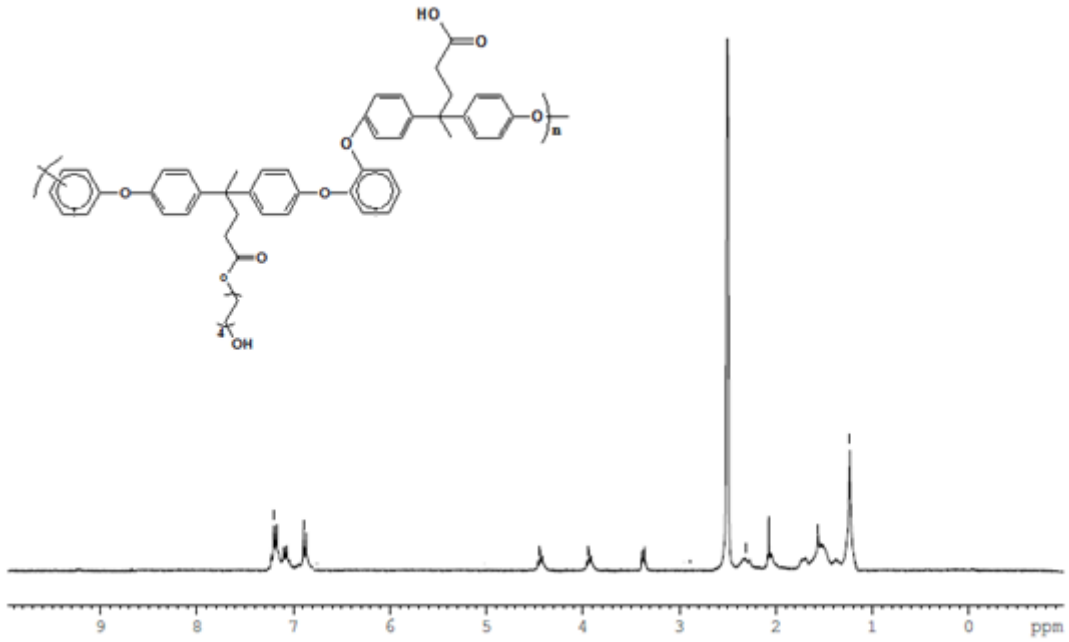


Figure 3.21: ^{1}H NMR of compound **3.11** in DMSO-d_6**.**

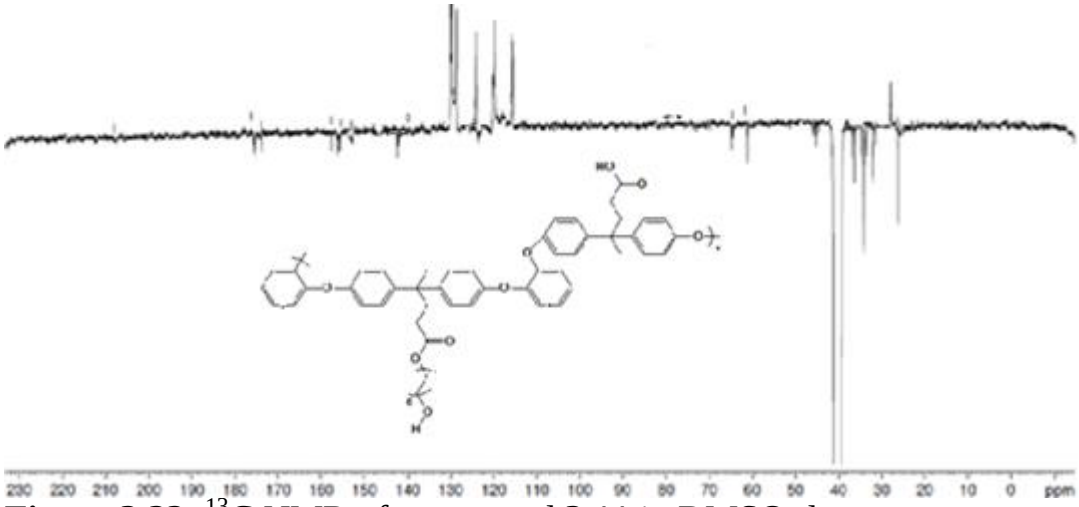


Figure 3.22: ^{13}C NMR of compound **3.11** in DMSO-d_6

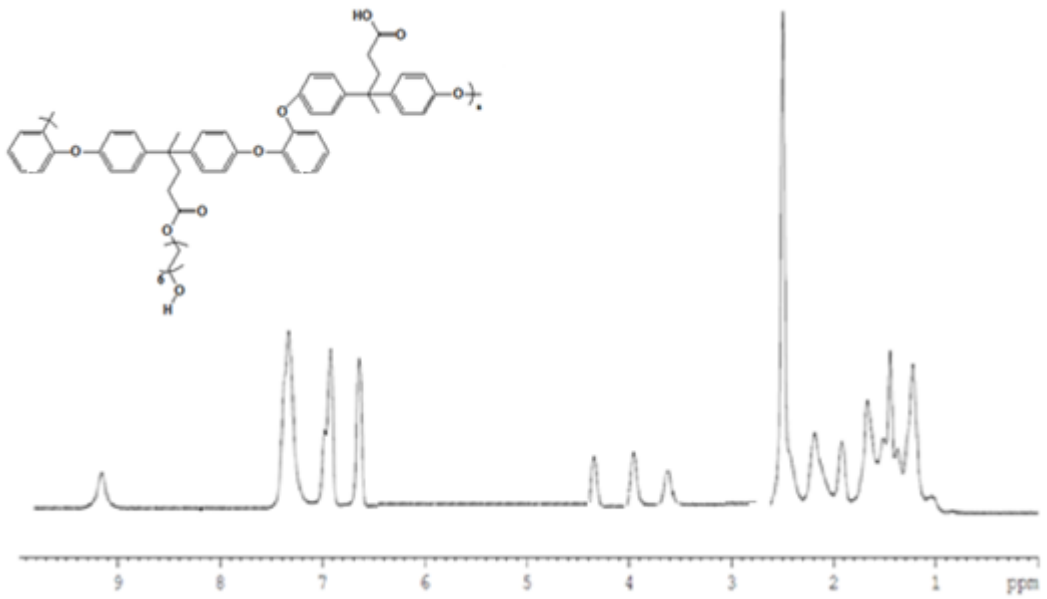


Figure 3.23: ^{1}H NMR of compound **3.12** in DMSO-d_6**.**

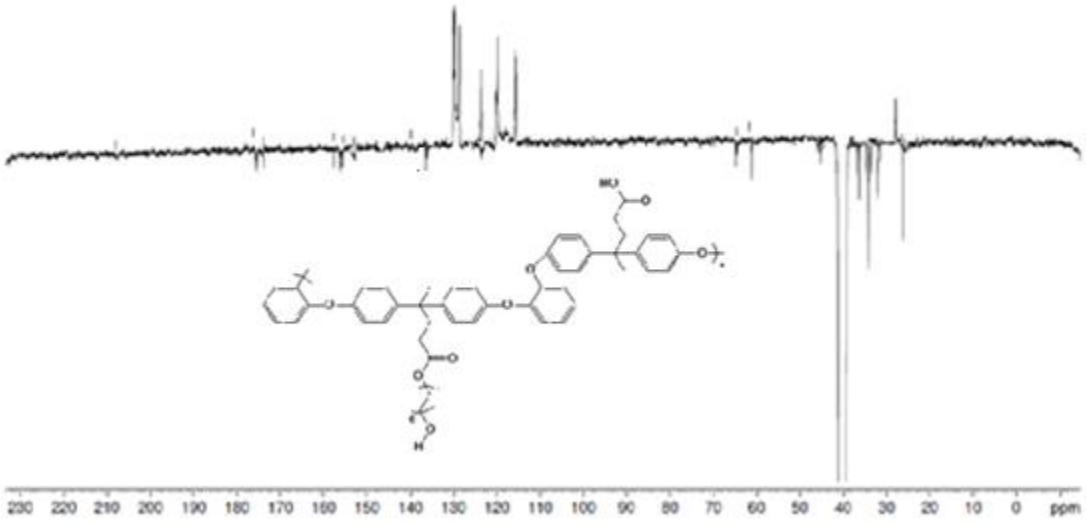


Figure 3.24: ^{1}H NMR of compound **3.12** in DMSO-d_6**.**

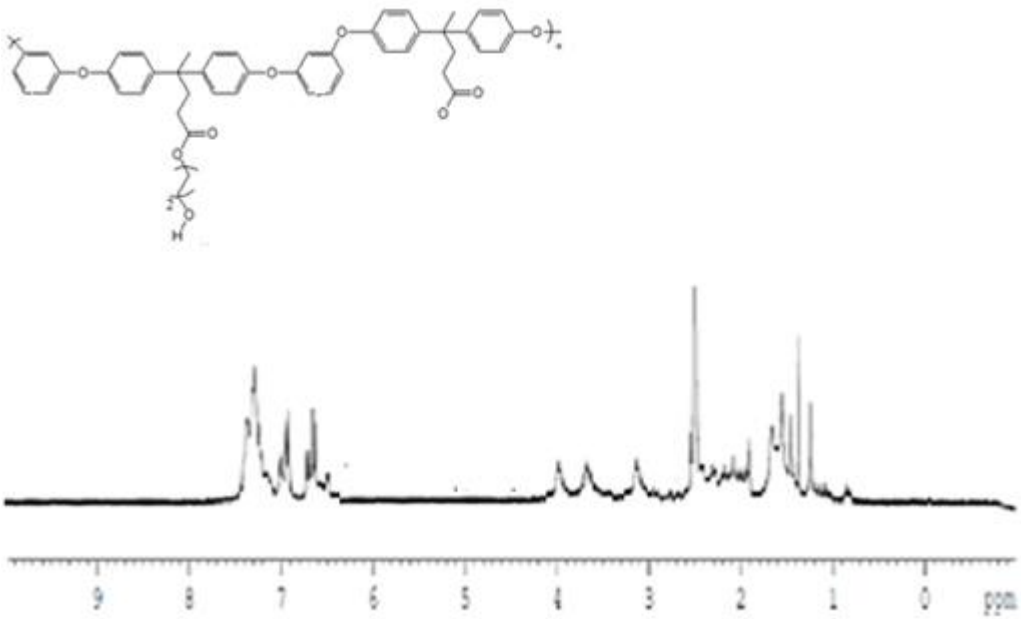


Figure 3.25: ^{1}H NMR of compound **3.13** in DMSO-d_6**.**

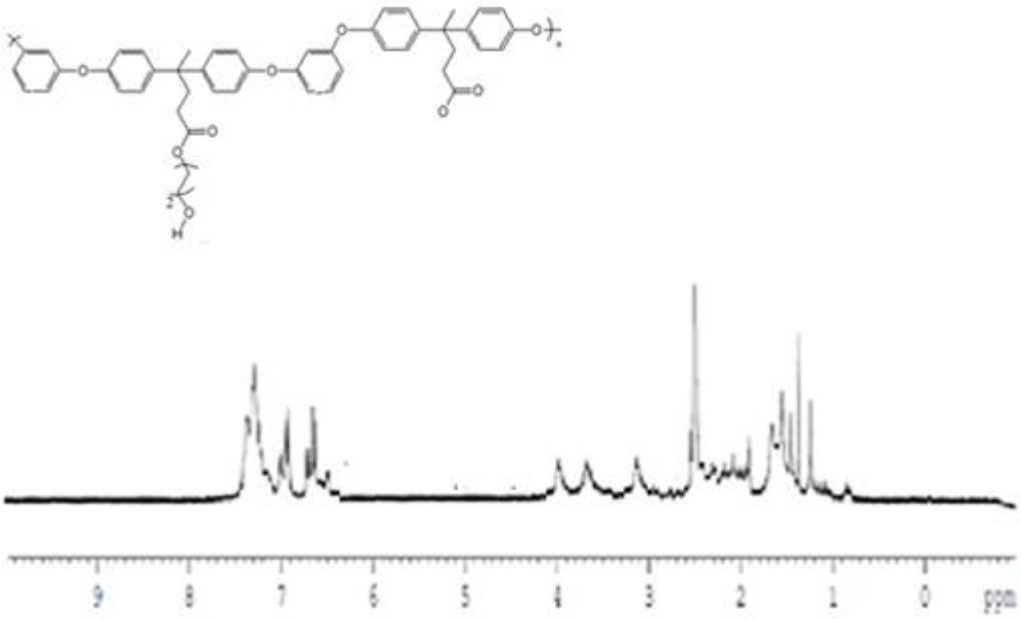


Figure 3.26: ^{13}C NMR of compound **3.13** in DMSO-d_6**.**

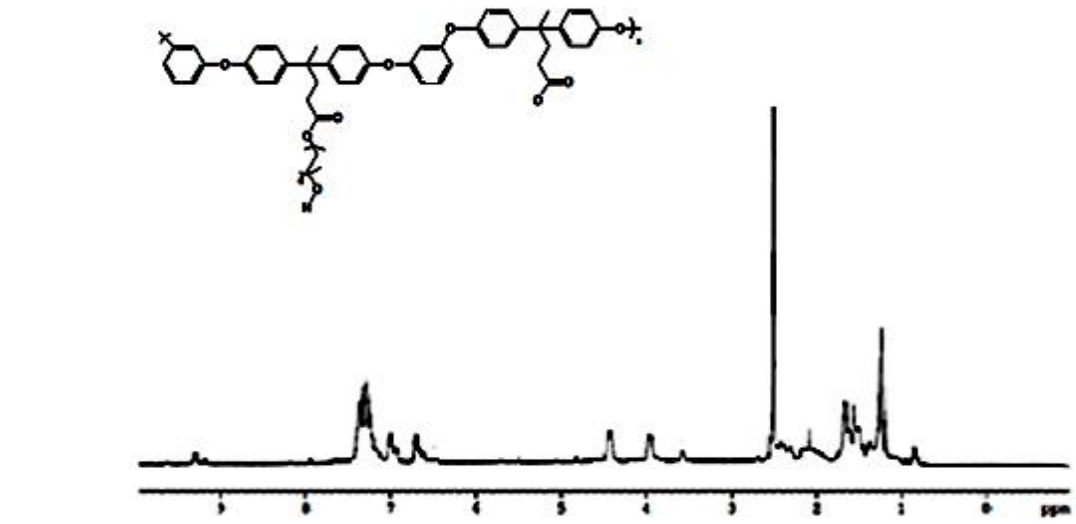


Figure 3.27: ^{1}H NMR of compound **3.14** in DMSO-d_6**.**

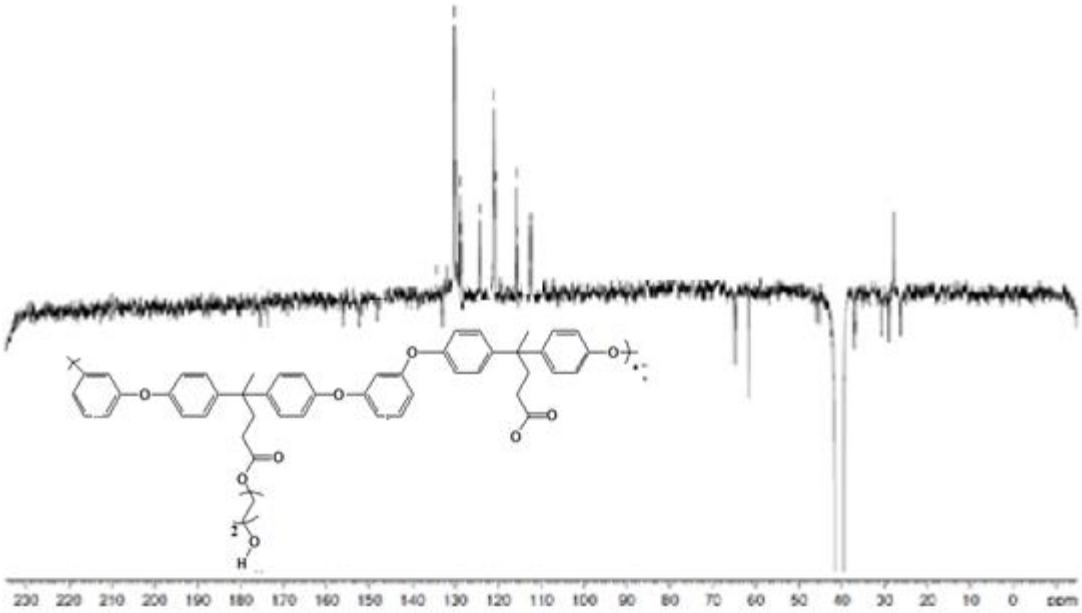


Figure 3.28: ^{13}C NMR of compound **3.14** in DMSO-d_6**.**

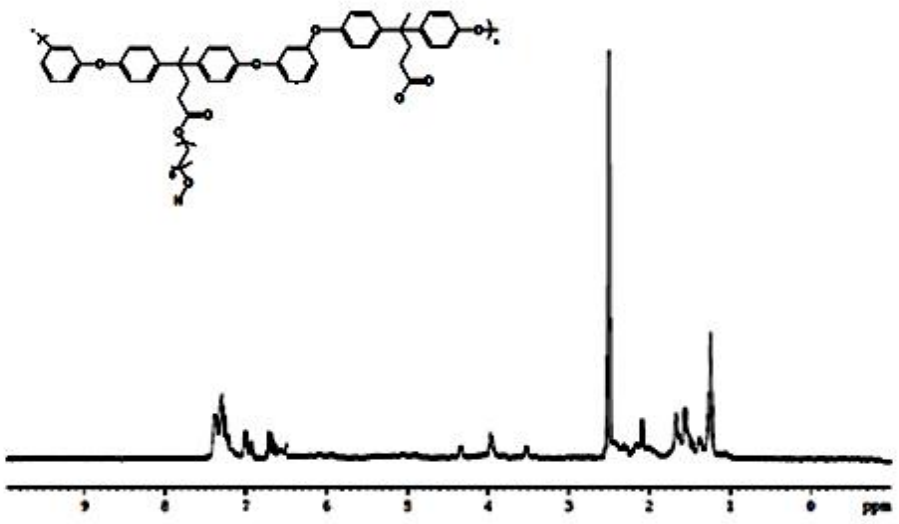


Figure 3.29: ^{1}H NMR of compound **3.15** in DMSO-d_6**.**

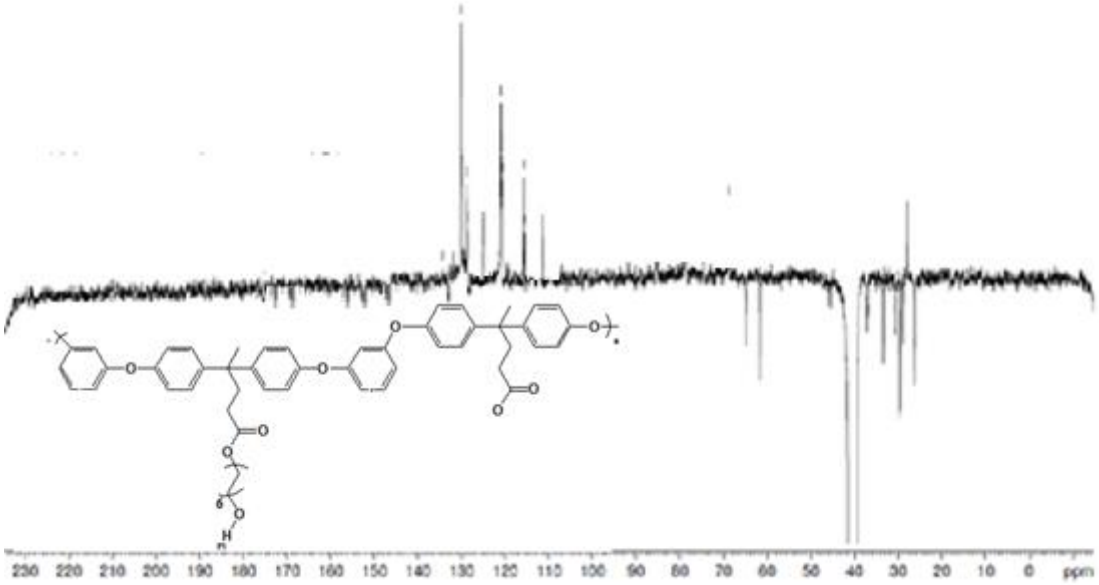


Figure 3.30: ^{13}C NMR of compound **3.15** in DMSO-d_6**.**

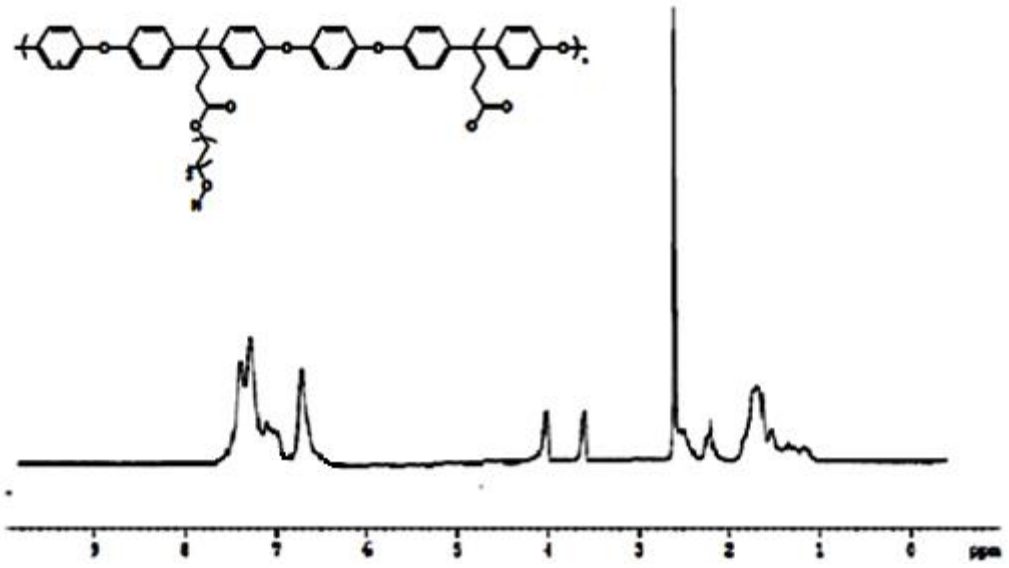


Figure 3.31: ^{1}H NMR of compound **3.16** in DMSO-d_6**.**

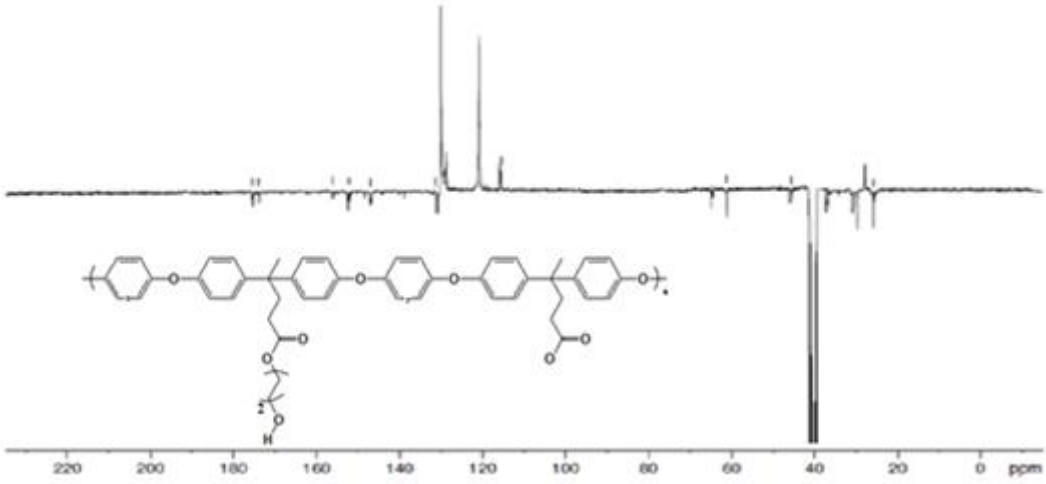


Figure 3.32: ^{13}C NMR of compound **3.16** in DMSO-d_6**.**

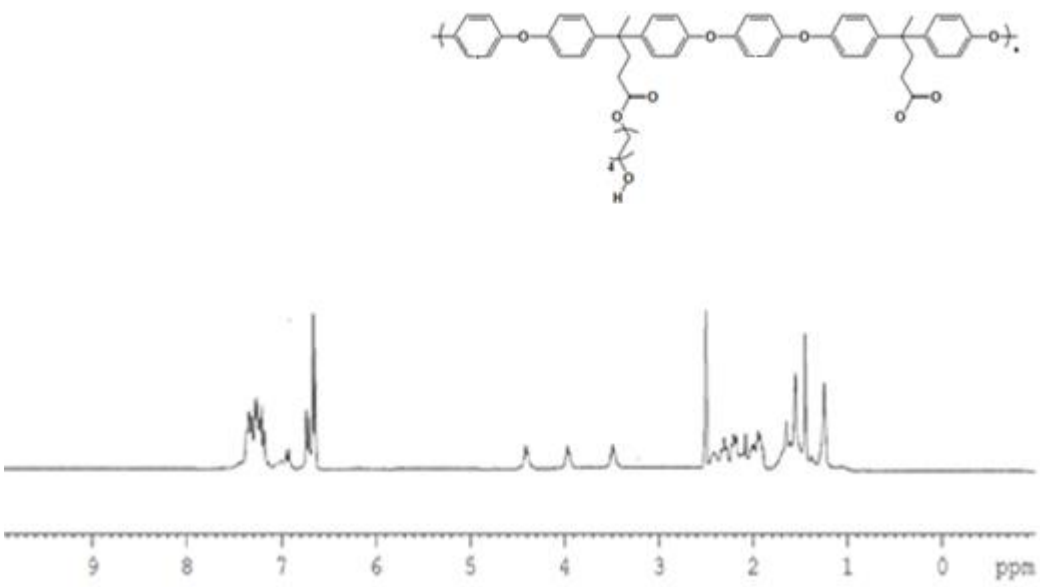


Figure 3.33: ^{1}H NMR of compound **3.17** in DMSO-d_6**.**

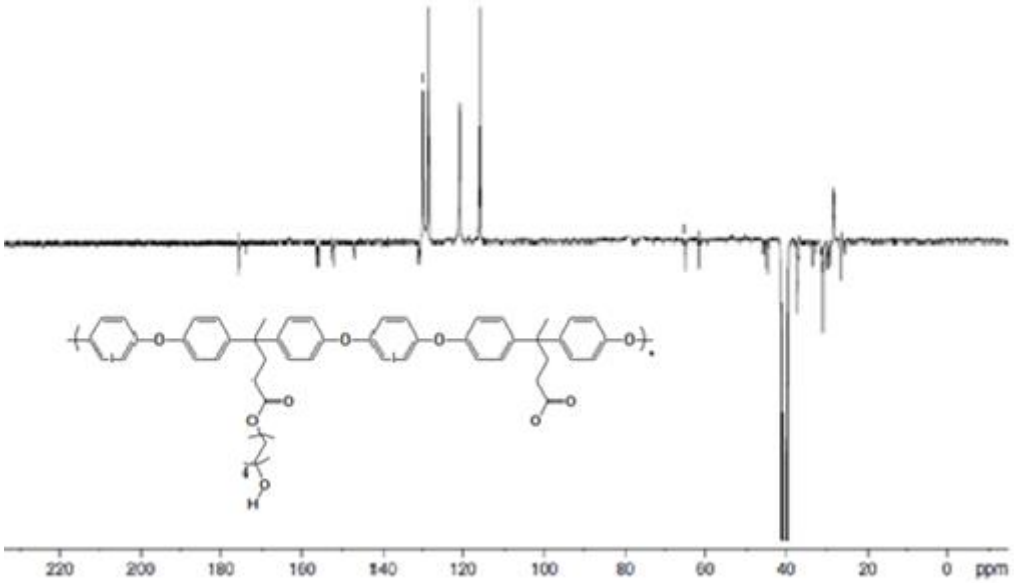


Figure 3.34: ^{13}C NMR of compound **3.17** in DMSO-d_6**.**

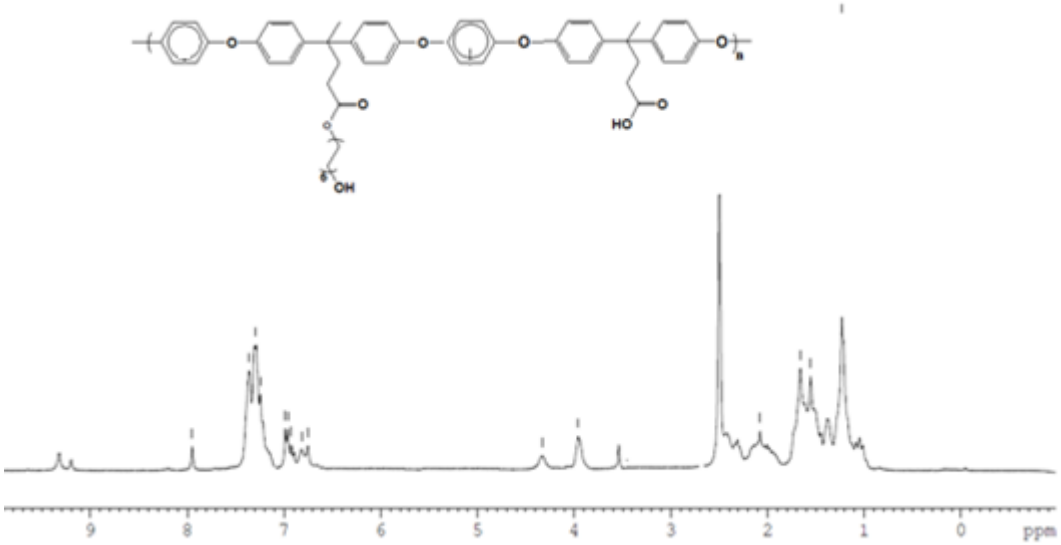


Figure 3.35: ^{1}H NMR of compound **3.18** in DMSO-d_6**.**

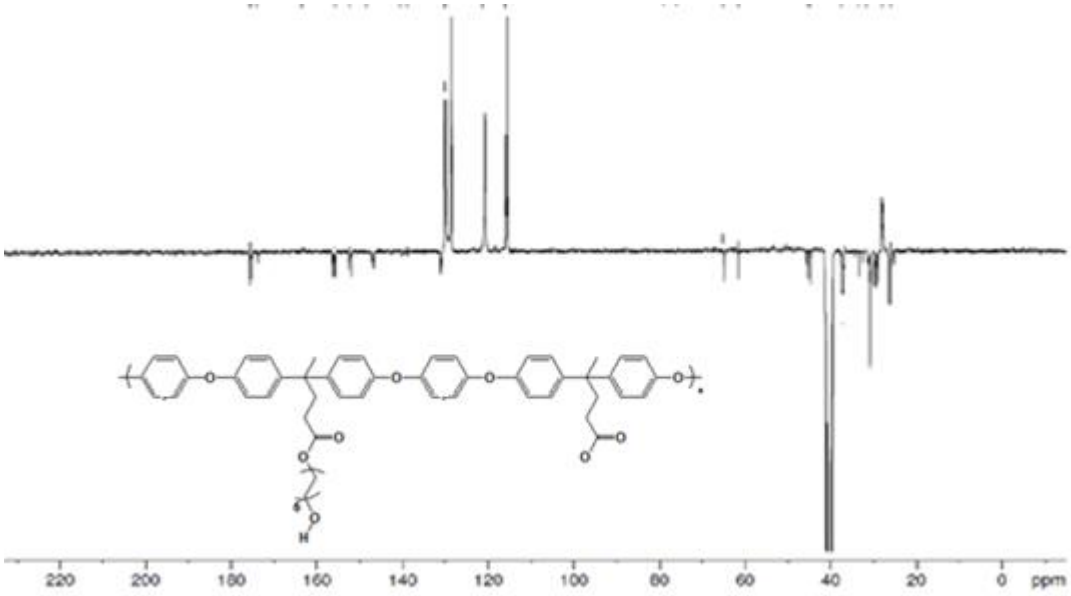


Figure 3.36: ^{13}C NMR of compound **3.18** in DMSO-d_6**.**

Table 3.03: ^{1}H NMR Analysis of compounds **3.10-3.18** in DMSO d_6

Compound	Aromatic Protons	Others
3.10 ^{1}H	6.80 (S, 2H,) 6.87(S, 2H) 7.37(M, 8H)	1.26-1.78(10H) 1.93(S, 4H) 2.50(S, 4H) 3.50(S,1H) 3.95(S,2H) 4.50 (S.2H)
3.11 ^{1}H	6.72 (S, 2H) 6.87(S,2H) 7.10(M,8H)	1.30-1.76(M,18H) 1.93(S,4H) 2.2(S,4H) 3.45(S,1H) 3.95(S,2H) 4.43 (S.2H)
3.12 ^{1}H	6.43 (S, 2H) 6.77(S, 2H) 7.11(M,8H)	1.22-1.76(M,26H) 1.93(S,4H) 2.28(S,4H) 3.45(S,2H) 3.95(S, 2H) 4.47 (S.2H)
3.13 ^{1}H	6.73 (S, 1H,S) 6.97(S, 2H) 7.28(M, 8H)	1.3-1.8(M,10H) 2.00(S, 4H) 2.5(S, 4H) 3.5(S, 2H) 3.95(S, 2H) 4.50 (S.1H)
3.14 ^{1}H	6.65(M,2H) 6.98 (S,2H) 7.17(M,8H)	1.3-1.8(M,18H) 1.95(S, 4H) 2.5(S, 4H) 3.5(S, 1H) 3.95(S, 2H) 4.5 (S.2H)
3.15 ^{1}H	6.65(2H,M) 6.95 (2H,S) 7.20(M,8H)	1.30-1.80(M,26H) 1.95(S, 4H) 2.5(S, 4H) 3.5(S, 1H) 3.95(S, 2H) 4.50 (S.2H)
3.16 ^{1}H	6.68(8H,S) 7.23(M,8H)	1.20-1.80(M, 10H) 2.1(S, 4H) 2.5(S, 4H)

		3.5(S, 1H) 3.95(S, 2H) 4.53 (S,2H)
3.17 ^{1}H	6.82(S, 4H) 7.20(M, 8H)	1.2-1.8(M, 18H) 2.32(S, 4H) 2.6(S, 4H) 3.44(S, 1H) 3.97(S, 2H) 4.25 (S.2H)
3.18 ^{1}H	6.85(S, 8H) 7.15 (M, 8H)	1.2-1.8(M, 28H) 2.32(S, 4H) 2.6(S, 4H) 3.44(S, 2H) 3.97(S, 2H) 4.25 (S.1H)

Table 3.04: ^{13}C NMR Analysis of compounds 3.10-3.18 in DMSO d_6

Compound	Aromatic Carbon	Others
3.10 ^{13}C	117.88 121.22 126.44 125.72 129.70 131.03 143.92 155.38 157.69	26.33 27.9 29.8 31.9 37.2 45.43 61.5 64.52 173.8 176.128
3.11 ^{13}C	117.78 121.24 126.34 125.72 129.67 131.03 143.90 155.40 157.72	26.44 27.22 27.80 33.90 38.20 44.94 61.50 64.52 173.80 176.18
3.12 ^{13}C	117.60 121.28 126.24 125.23 129.63 131.09 143.82 155.31 157.45	26.33 27.90 29.8 31.90 37.20 45.43 61.50 64.52 173.8 176.128
3.13 ^{13}C	116.12 119.21 122.32 125.78 129.23 130.70 143.23 153.40 156.80	25.59 27.32 31.90 38.11 43.94 61.67 64.52 173.67 175.13

3.14 ^{13}**C**	116.22 119.31 122.32 125.67 129.43 130.44 143.11 153.21 157.12	26.44 27.22 28.30 33.90 38.20 44.94 61.45 64.52 173.80 176.12
3.15 ^{13}**C**	117.92 119.21 123.12 125.78 128.93 130.68 143.23 153.43 156.92	26.21 22.98 28.21 32.90 39.43 44.94 61.54 64.7 173.22 176.21
3.16 ^{13}**C**	116.72 122.73 131.31 132.83 133.72 149.84 154.31 156.91	27.98 31.60 31.60 37.53 61.56 65.18 174.15 175.47
3.17 ^{13}**C**	116.32 122.23 131.87 132.76 133.23 149.12 154.25 156.17	26.08 27.90 29.50 31.55 37.53 45.10 61.56 65.18 174.15 175.47
3.18 ^{13}**C**	116.77 122.23 131.20 132.89 133.32 149.21 154.52 156.71	26.08 27.22 29.33 31.35 37.53 45.22 61.43 65.18 174.23 175.34

3.4 Thermal Properties of the Polymeric Ether.

The thermal properties of the cationic and neutral organoiron polymers were studied using thermogravimetric analysis (TGA) As anticipated, polymers containing cyclopentadienyliron cations coordinated to arenes in their backbones experienced weight losses of approximately 17 to 33% between 219 and 260 $^{\circ}$C due to the loss of the pendent iron complexes. Additional weight loss steps were observed starting at 343 °C and 465 °C, which were attributed to degradation of the polymer backbones. Figure 3.37 shows the TGA thermogram of mixed charge organoiron polymer 3.02.

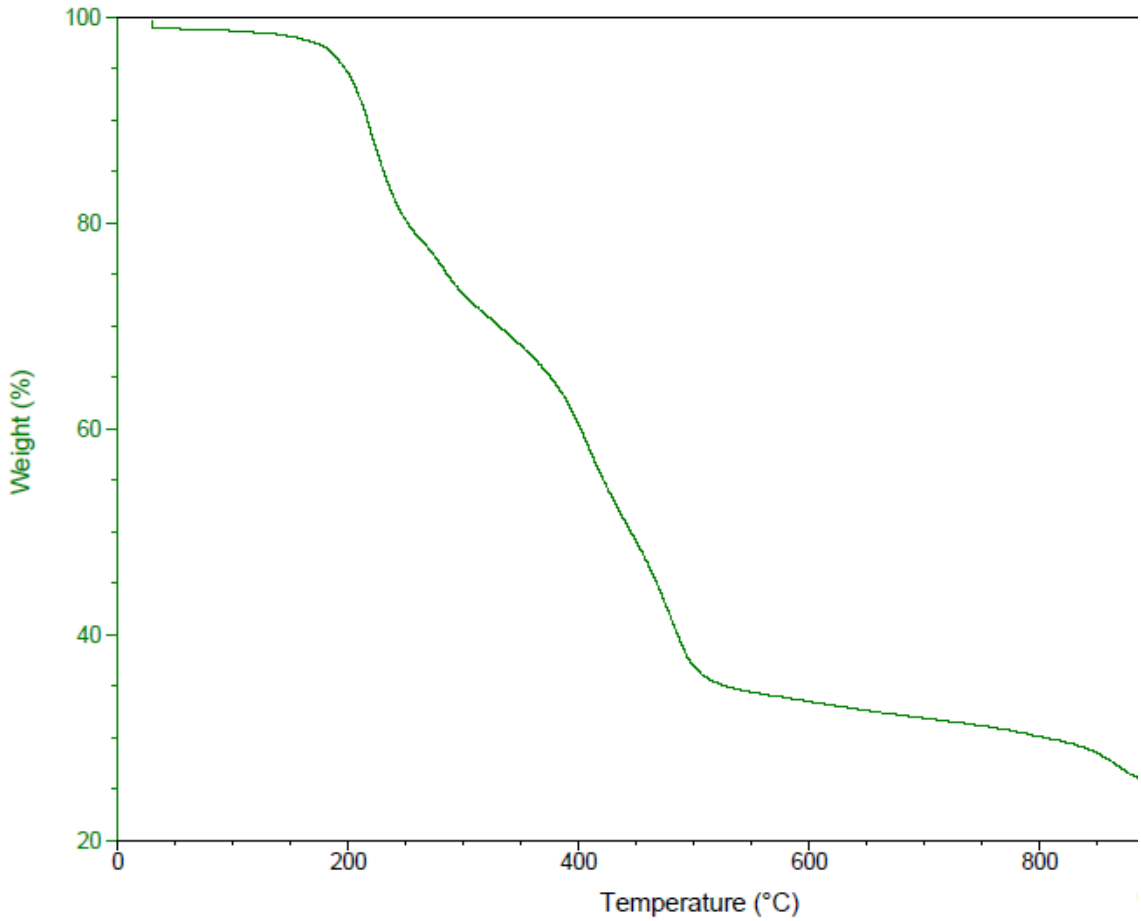


Figure 3.37: Thermogram of Polymer **3.02** in nitrogen

3.5 Scanning Electron Microscopy

The surface texture as illustrated in a powder film was investigated for the series of complexes by scanning electron microscopy. Representative surface morphology of the films is shown in Figure 3.20.

An SEM image for complex **3.01** displayed highly irregular surface morphology at low magnification. The micrographs of complexes **3.02** had particles demonstrating a fine globular appearance (Figure3.20). Complex **3.03**

appeared as distinct layer with smooth edges and some pores were observed, with the particles possessing a rock-like appearance at lower magnification.

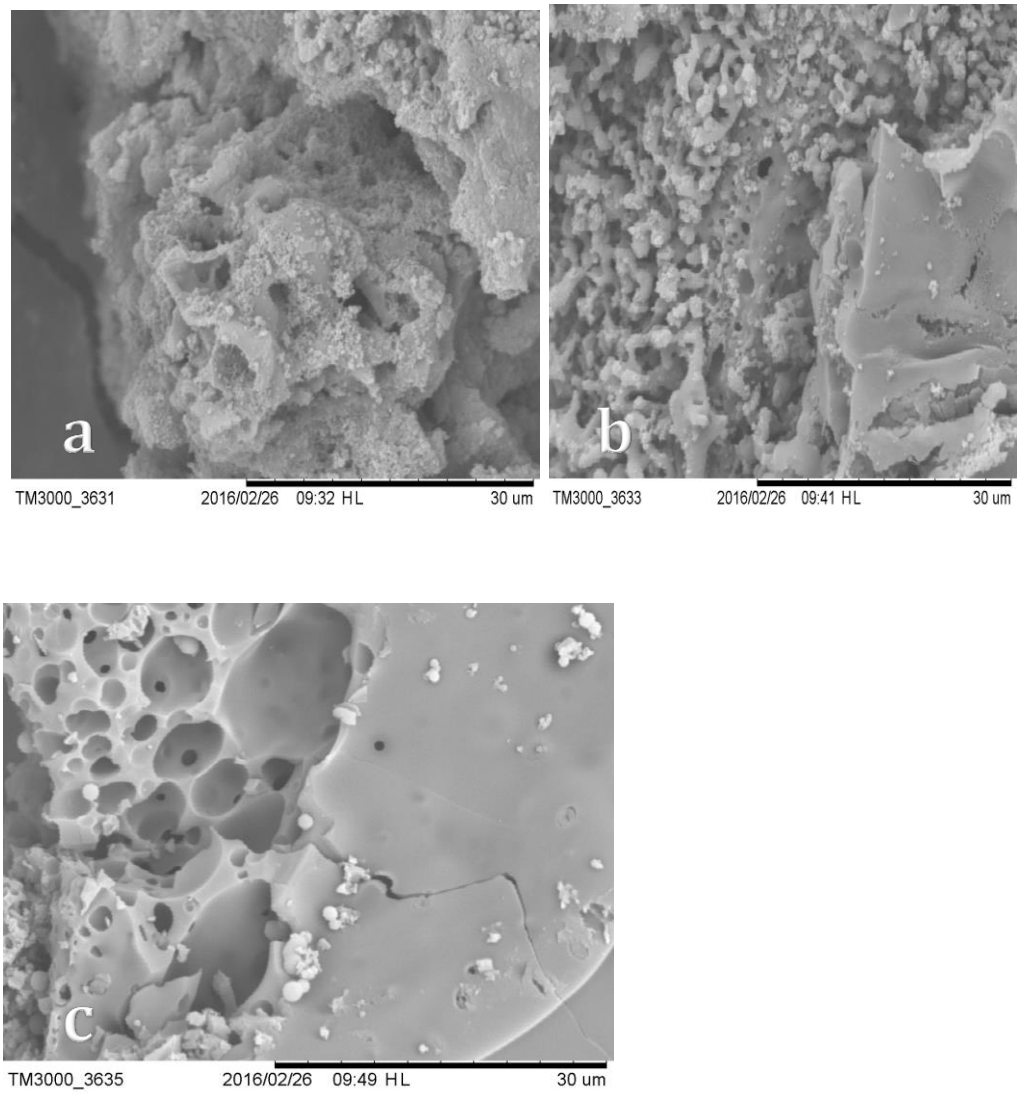


Figure 3.38: Scanning electron micrographs of a**) 3.01,**b) **3.02** and c) **3.03** complexes.

Chapter 4. Experimental

4.1 Materials

Ammonium hexafluorophosphate, 4,4-bis (4-hydroxyphenyl) valeric acid, 1,4-butanediol, 1,8-octanediol, 1,12 dodecanediol, potassium carbonate, 4-(4-(dimethylamino) pyridine (DMAP),N,N'-Dicyclohexylcarbodiimide (DCC), anhydrous aluminum chloride, aluminum powder, ferrocene, 1,2-dichlorobenzene, 1,3- dichlorobenzene, 1,4- dichlorobenzene, and polyethene glycol and all reagent grade solvents are commercially available and were used without further purification.

4.2 Characterization.

Instrumentation. A Bruker Avance NMR spectrometer (1 H, 300 MHz; 13C, 75 MHz; 11B, 96 MHz; and 31P, 122 MHz) was used to record the ^{1}H, ^{13}C, and spectra of all synthesized compounds. All spectra were acquired using DMSO-d_6. For ^{1}H and ^{13}C, the chemical shifts were internally referenced to the DMSO-d_6 residue peak. e. The scanning electron micrographs (SEM) of the complexes were obtained on a Hitachi TM3000 SEM.

4.3. Synthetic methodology

4.3.1 Ligand Exchange Reactions

Starting complexes **2.01-2.03,** were synthesized according to earlier publications.[38] In a 500 mL, 3-necked round bottom flask were placed 28.32 g (152.20 mol) ferrocene, 41.42 g (310.6 mol) aluminum chloride, 4.4 g (163 mol) aluminum, and a 4-fold excess of the appropriate arene. The reaction mixture was heated at 135-140 °C for five hours under a nitrogen atmosphere. The green-black mixture was then cooled to approximately 80°C upon which time it was poured slowly (this is an extremely vigorous reaction) into 500 mL of an ice-water slurry. The resulting aqueous mixture was then filtered through sand, and the filtrate washed with petroleum ether (3 x 50mL,) and diethyl ether (3 x 50 mL) to remove starting materials. To the aqueous layer was combined 13.9g (75 mmol) NH_4PF_6 to precipitate the product as a yellow-green solid. This material was redissolved in dichloromethane, and the water layers were also extracted with dichloromethane until it was virtually colorless. At this time, the combined dichloromethane solution was dried over $MgSO_4$, filtered, and concentrated by rotary evaporation to roughly 25 mL. Diethyl ether was then added to precipitate the desired product as a yellow-green material which was collected by vacuum filtration, rinsed with diethyl ether, and dried before analysis.

4.3.2 Synthesis of Complexes 2.04-2.06

Isomeric the η^6-dichlorobenzene-η^5-cyclopentadienyliron (II) hexafluorophosphate complex (3.39g, 8.21mmol), 4,4-Bis (4-hydroxyphenyl) valeric acid (1.101g, 3,84mmol) acid and K_2CO_3 (3.25g, 23.54mmol) were stirred in a 50mL round bottom flask under nitrogen atmosphere for 3 days to ensure both phenolic groups are metal-mediated due to the ratio of the reagents. Ammonium hexafluorophosphate (1.33g, 8.1mmol) was added to this solution. The resulting precipitate was collected in a sintered glass crucible and washed with water. The complex was then washed with diethyl ether and dried under reduced pressure.

4.3.3. Synthesis of 2.07, 2.10, 2.13 Compounds.

Isomeric of -bis (η^6-dichlorobenzene-η^5-cyclopentadienyliron) 4,4-bis(4-hydroxyphenyl) valeric acid hexafluorophosphate complexes (2.1-2.5) (1.039g, 1mmol) with 1,4butandiol (0.090g, 1mmol), DCC (0.412g, 2mmol) and DMAP (0.244g, 2mmol) were stirred with 10mL of DMF under N_2 for 24h. The mixture was placed in a freezer to precipitate DCU and was then poured into 10% HCl with ammonium hexafluorophosphate amount. The resulting participate was collected in a sintered glass crucible and washed with methanol many times to remove any remaining DCU. The product was collected and dried under reduced pressure with yields 74-90%.

4.3.5. Synthesis of 2.08 , 2.11, 2.14 Compounds.

Isomeric of -bis(η^6-dichlorobenzene- η^5-cyclopentadienyliron) 4,4- bis (4-hydroxyphenyl) valeric acid hexafluorophosphate (1.039g, 1mmol) with 1,8 octanediol (0.0146g, 1mmol), DCC (0.412g, 2mmol) and DMAP (0.244g, 2mmol) were stirred with 10mL of DMF under N_2 for 24h. The mixture was placed in a freezer to precipitate DCU and then was poured into 10% HCl with ammonium hexafluorophosphate amount. The resulting precipitate was collected in a sintered glass crucible and washed with methanol many times to remove any remaining DCU. The product was collected and dried under reduced pressure with yields 74-90%.

4.3.6. Synthesis of 2.09, 2.12, 2.15. Compounds.

Isomers of -bis *(*η^6-dichlorobenzene-η^5-cyclopentadienyliron) 4,4- bis (4-hydroxyphenyl) valeric acid hexafluorophosphate (1.039g, 1mmol) 1,12 dodecanediol (0.202g, 1mmol), DCC (0.412g, 2mmol) and DMAP (0.244g, 2mmol) were stirred with 10mL of DMF under N_2 for 24h. The mixture was placed in a freezer to precipitate DCU and then was poured into 10% HCl with ammonium hexafluorophosphate amount. The resulting precipitate was collected in a sintered glass crucible and washed with methanol many times to

remove any remaining DCU. The product was collected and dried under reduced pressure with yields 74-90%.

4.3.7. Synthesis of Polymetallic complexes.

These complexes were prepared by using 1:1 molar ratio of complexes to nucleophile with excess of base (K_2CO_3) and DMF as a solvent. After stirring magnetically under nitrogen atmosphere for 24h the desired complexes were isolated in the same manners as the previously desired bimetallic complexes.

4.3.7.1. Synthesis of 3.01, 3.04, 3.07 Compounds.

Complexes **3.01, 3.04, 3.07** with terminal chlorine atoms (0.27mmol, 0.3g), 4,4- Bis (4-hydroxyphenyl) valeric acid (0.27mmol, 0.0772g), K_2CO_3 (0.675 mmol, 0.09g), were stirred with 0.5 mL of DMF. The dark red solutions were magnetically stirred under a nitrogen atmosphere for 24h. The reaction mixture was then added to 10% HCl solution with ammonium hexafluorophosphate. The resulting precipitate was collected in a sintered glass crucible and washed with water. The polymetallic complexes were then washed with diethyl ether and dried under reduced pressure.

4.3.7.2. Synthesis of 3.02, 3.05, 3.08 Compounds.

2.08, 2.11, 2.14 Compounds with terminal chlorine atoms (0.314mmol, 0.3g), 4,4- Bis (4-hydroxyphenyl) valeric acid (0.27mmol, 0.0772g), K2CO3 (0.675 mmol, 0.09g), and 0.5 mL of DMF. The dark red solutions were magnetically stirred under a nitrogen atmosphere for 24h. The reaction mixture was then added to 10% HCl solution and ammonium hexafluorophosphate. The resulting participate was collected in a sintered glass crucible and washed with water. The Polymetallic complexes**.**were then washed with diethyl ether and dried under reduced pressure.

4.3.7.3 Synthesis of 3.03, 3.06, 3.09. Compounds.

2.09, 2.12, 2.15 Compounds with terminal chlorine atoms (0.33 mmol, 0.3g), 4,4- Bis (4-hydroxyphenyl) valeric acid (0.27mmol, 0.0772g), and K_2CO_3 (0.675 mmol, 0.09g), were stirred with 0.5 mL of DMF. The dark red solutions were magnetically stirred under a nitrogen atmosphere for 24h. The reaction mixture was then added to 10% HCl solution and ammonium hexafluorophosphate. The resulting precipitate was collected in a sintered glass crucible and washed with water. The polymetallic complexes**.**were then washed with diethyl ether and dried under reduced pressure.

Chapter 5. Conclusion and future work.

The versatility of $CpFe^+$ mediated aromatic nucleophilic substitution in the design of a variety of isomeric bimetallic complexes has been demonstrated by incorporation of oxygen containing linkages. Aromatic dinucleophiles were reacted with various isomeric cyclopentadienyliron complexes of chloroarene to yield the corresponding bis (cyclopentadienyliron) arene dications. These bis (cyclopentadienyliron) arenes were reacted with different length of diols. It was found that the solubility increases as the length of diols increase. For instance, isomers of bis (cyclopentadienyl iron) arene complexes were reacted with PEG, and it was found these complexes were soluble even in the water. These complexes were also characterized by analytical and spectroscopic technique.

The versatility of $CpFe^+$ for this new method allowed for a series of polymetallic ethers complexes to be prepared. The isomers of bis (cyclopentadienyliron) arene complexes with terminal chloroarene were reacted with 4,4- bis (4-hydroxyphenyl) valeric acid bimetallic. It was noted that the polymers, with shorter length diols were difficult to dissolve in common solvents except for DMSO. However, increasing the length of diols leads to enhanced solubility. For example, some compounds (3.15) were totally soluble in common solvents such as acetone.

The efficient removal of the metallic moieties via photolytic demetallation resulted in the liberation of the organic compounds under very mild conditions. This procedure offers one of the most general and least expensive routes to a variety of complexes and compounds, which may be of great interest in material science.

The goal of this work is to create water soluble polymers. In chapter 2, three different complexes are prepared and these complexes showed a great deal of solubility not only in different organic solvents but also in aqueous media. The increase of the carboxylic acid groups with the long aliphatic chain showed improvements such as increased water solubility and improved surfactant compatibility. Hence, our procedure for synthesizing these soluble polymers is a focus of interest in the future work through the improvement of monomer and polymer structures to produce micelles. The mild conditions due to the incorporation of the organoiron complexes into polymeric structures and the ease of demetallation to obtain the purely organic polymers in good yield make this kind of polymerworthy of future attention. This class of monomeric and polymeric complexes could be used in many fields such as drug delivery and can be targeted to tumor sites which may act as a vehicle for antitumor drugs.

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